A Study of Hydrocarbon Reactions over Supported Metal Catalysts : Support and Metal Dependence

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ABSTRACT

The effects of using the reducible oxide supports, TiO_2 and Nb_2O_5, on the catalytic properties of rhodium and platinum have been investigated. A more extensive study of hydrocarbon exchange mechanisms effected by the group VIII metals platinum, rhodium, iridium and palladium supported on various supports has also been carried out. This latter study, as well as using conventional techniques of gas chromatography and mass spectrometry, utilised ^2D nmr. This technique allows the identification and estimation of various possible groupings of deuterium atoms in several alkanes and alkenes.

Platinum and rhodium catalysts supported on Nb_2O_5 (1% loading), and a 1 wt.% Pt/TiO_2 sample for comparison, were prepared and characterised by temperature-programmed techniques. The hydrogenolysis of 2-methylbutane was used as a test reaction to measure the activity of the catalysts after reduction at 523K (LTR treatment) and at 773K (HTR treatment). Exchange of 2-methylbutane with deuterium over Pt/Nb_2O_5 was also investigated. The results from both platinum catalysts after LTR proved to be similar to those reported for an alumina-supported sample. The rhodium catalyst was more active for hydrogenolysis than the platinum catalysts. After HTR the activity for hydrogenolysis was suppressed by factors of 10, 600 and 10^5 for Pt/TiO_2, Pt/Nb_2O_5 and Rh/Nb_2O_5

respectively due to strong metal-support interactions (SMSI). The exchange reaction was more affected by SMSI than the hydrogenolysis reaction. Dehydrogenation was found to occur over HTR Pt/Nb_2O_5 only.

Using ^2D nmr the exchange reactions of propane, 2-methylpropane, butane, 2-methylbutane, 2,2-dimethylpropane (DMP), 2,2,3,3-tetramethylbutane (TMB) and 2,2,4,4-tetramethylpentane (TMP), as well as the exchange and addition reactions of 2-methylpropene with deuterium were investigated. With the less branched alkanes the results from both platinum and palladium could be explained by interconversion of adsorbed alkyl and alkene intermediates; results from rhodium however could only be explained if 1,3-diadsorbed species were invoked. The results from the iridium catalyst were dominated by stepwise exchange on the alumina support. A comparative study using the more branched alkanes DMP, TMB and TMP at 400K showed that four processes contributed to different extents with the various hydrocarbon-metal systems. These were (I) stepwise exchange, (II) methyl group exchange, and more general multiple exchange involving (III) $\alpha\gamma$-diadsorbed or (IV) $\alpha\delta$-diadsorbed intermediates.

Exchange of 2-methylpropene over palladium was faster than the addition reaction and the deuterium atoms were randomly distributed in the alkene, probably through a π-allyl dissociative mechanism. With platinum and rhodium exchange occurred preferentially in the methylene groups

of the alkene and the results indicated that exchange involved adsorbed vinyl intermediates together with some intramolecular double-bond movement. Relatively little exchange occurred with iridium. The activities of the metals for production of alkane at 235K were Rh>Ir>Pd>Pt. With all metals except palladium further exchange occurred during the addition process, this was found to be concentrated in one methyl group. This behaviour was explained in terms of mechanisms that permitted additional exchange of the methylene group to take place during the addition process.

I certify that, unless otherwise stated, all the work described in this thesis was performed by myself in the laboratories of the University of Edinburgh in the period from September 1985 to September 1988.

Ronald Brown

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CHAPTER 1

SUPPORTED METAL CATALYSTS

1.1 INTRODUCTION

Metal catalysts are used widely in the chemical and petroleum industries for the manufacture of products of great interest to everyone. Examples of their applications range from petroleum refining, fat hardening to the treatment of vehicle exhaust emission. Research on metal catalysts and on the surface processes involved in metal-catalysed reactions has contributed greatly to the development of heterogeneous catalysis.

In heterogeneous catalysis studies are made of the influence of substances on the rates of chemical reactions with the catalyst being in a different phase from the reactants, normally a solid. The definition of a catalyst as "a substance which increases the rate of chemical reaction without itself undergoing a chemical change" has remained unchanged since first proposed by Ostwald in 1894[1]. In order to understand the mechanism by which a catalyst works it is useful to look at a specific case. The water gas shift reaction

$$H_2O + CO \rightarrow H_2 + CO_2$$

which is used in the production of hydrogen in several commercial processes is catalysed by iron and chromium oxides. A simplified scheme for the reaction can be written as

$$H_2O + * \rightarrow H_2 + O* \quad (i)$$

$$CO + O* \rightarrow CO_2 + * \quad (ii)$$

where the asterisk, *, represents an empty catalytic site. Thus water reacts with the catalyst to produce hydrogen and a highly reactive oxygen intermediate, which then reacts with CO to produce CO_2 and to regenerate the catalytically active site, *. The potential energy curve associated with this process is shown schematically in figure 1.1. The full line depicts the variation of potential energy of the homogeneous reaction, while the dotted line is for the heterogeneous process. An

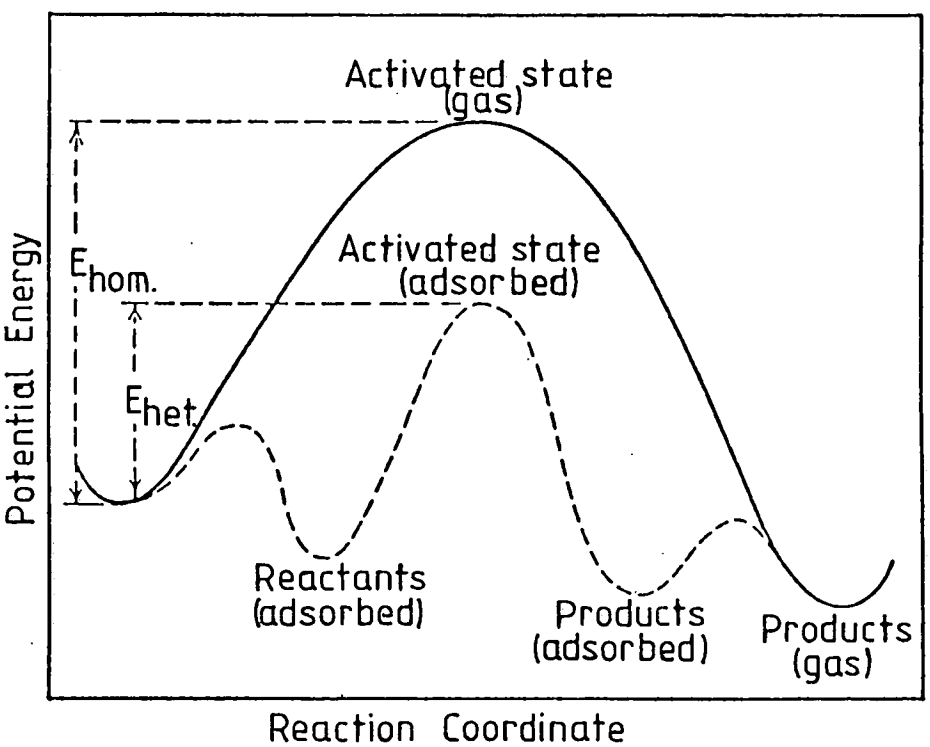

Figure 1.1 Potential Energy Curves for the water gas shift reaction: homogeneous and heterogeneous.

important aspect of the catalytic reaction is that it represents a cycle that occurs many times as the process proceeds. Each repetition of the cycle is called a turnover and a good catalyst will have a very large turnover number. Several points are important in any consideration of the energetics and reaction scheme. (i) The potential energy diagram, figure 1.1, shows that the heterogeneously catalysed reaction has a lower activation energy than the gas phase homogeneous reaction. This is the origin of the enhancement of the reaction rate and it applies both in the forward and reverse directions of the reaction. Table 1.1 illustrates some experimental results for a number of reactions which have been studied both as homogeneous and heterogeneous processes. (ii) As the ΔH_o of the reaction does not change for either process, the thermodynamic equilibrium between the reactants and products does not change. Catalysts increase the rate of approach to equilibrium but do not alter the thermodynamic equilibrium value itself. (iii) As shown by the overall reaction stoichiometry, there is no net consumption or production of the catalytic site, *. The reaction proceeds by repetition of the catalytic cycle with the catalytic species remaining unchanged at the end. (iv) The intermediate, O*, needs to be of intermediate stability. If it is too stable, it will not decompose, to form the product whereas if it is too unstable, it will not form in the first place.

Table 1.1

Activation Energies for Homogeneous and Heterogeneous Reactions

Decomposition of	Surface	$E_{het.}$	$E_{hom.}$
Hydrogen iodide	Gold	25.0 kcal.	44.0 kcal.
Hydrogen iodide	Platinum	14.0	44.0
Nitrous oxide	Gold	29.0	58.5
Nitrous oxide	Platinum	32.5	58.5
Ammonia	Tungsten	39.0	>80
Ammonia	Platinum	44.3	>80

1 kcal. ≡ 4.2 kJ

Generally, the main steps in a heterogeneously catalysed reaction can be divided into the following elementary steps:

1. diffusion of reactants to the surface
2. adsorption of reactants at the surface
3. chemical reaction on the surface
4. desorption of products from the surface
5. diffusion of products away from the surface.

These are consecutive steps, and if any one has a much slower rate than all the others it will become rate determining.

1.2 TERMINOLOGY AND BASIC CONCEPTS OF HETEROGENEOUS CATALYSIS

Before proceeding further it is appropriate to introduce some of the basic concepts and terminology[2] used

in heterogeneous catalysis in reference to supported metal catalysts.

Prior to a catalyst being used it is often subjected to various treatments. The terms pretreatment or activation are applied to these set of treatments. For metal-supported catalysts the pretreatment usually involves reduction in flowing hydrogen at an elevated temperature. The ability of the catalyst to convert reactants to products is called the activity of the catalyst. In metal-supported catalysts the active metal catalyst is often present as the minor component dispersed upon a support. This support may be catalytically inert but it may contribute to the overall catalytic activity. The accessibility of the atom of metal in supported metal catalysts depends upon the percentage of the total atoms of metal which are surface atoms. Thus the terms percentage exposed or dispersion are used. If this value is known activity may be expressed as a turnover frequency, meaning the number of molecules converted per unit time per active site.

A loss of catalytic activity may be caused by traces of impurities in the reacting system which combine with the active sites on the catalyst, this is called poisoning. If a product of the reaction causes poisoning, then the catalyst has undergone self-poisoning. These two phenomena may be reversible or irreversible, if the former then the catalytic activity may be restored by some method

of regeneration. Loss of the percentage of metal atoms exposed due to agglomeration of the metal particles, i.e. sintering, will also cause loss of catalytic activity. This could also change the relative rates of two or more competing reactions on a catalyst, hence its selectivity.

Perhaps the most important aspect of catalysis is specificity, i.e. the particular ability of a substance or closely related group of substances to catalyse a given type of transformation. Much has been learned about the specificity of metal catalysts from systematic studies of a reaction over a series of metals. For a given series of metal catalysts the pattern of activity variation from one metal to another depends on the nature of the reaction as does the variation of catalytic activities. These points are clearly demonstrated by results of studies of the hydrogenolysis of carbon-carbon bonds in simple molecules[3,4]. Striking differences in activity patterns are discovered when comparison is made of the group VIII noble metals as catalysts for (a) the hydrogenation of cyclopropane to propane and (b) the hydrogenolysis of ethane to methane. The catalytic activities of silica-supported metals are shown in figure 1.2. This shows that:-

(i) for the triad of metals comprising osmium, iridium and platinum the relative activity for cyclopropane hydrogenation is Os<Ir<Pt but for ethane hydrogenolysis it is Pt<Ir<Os,

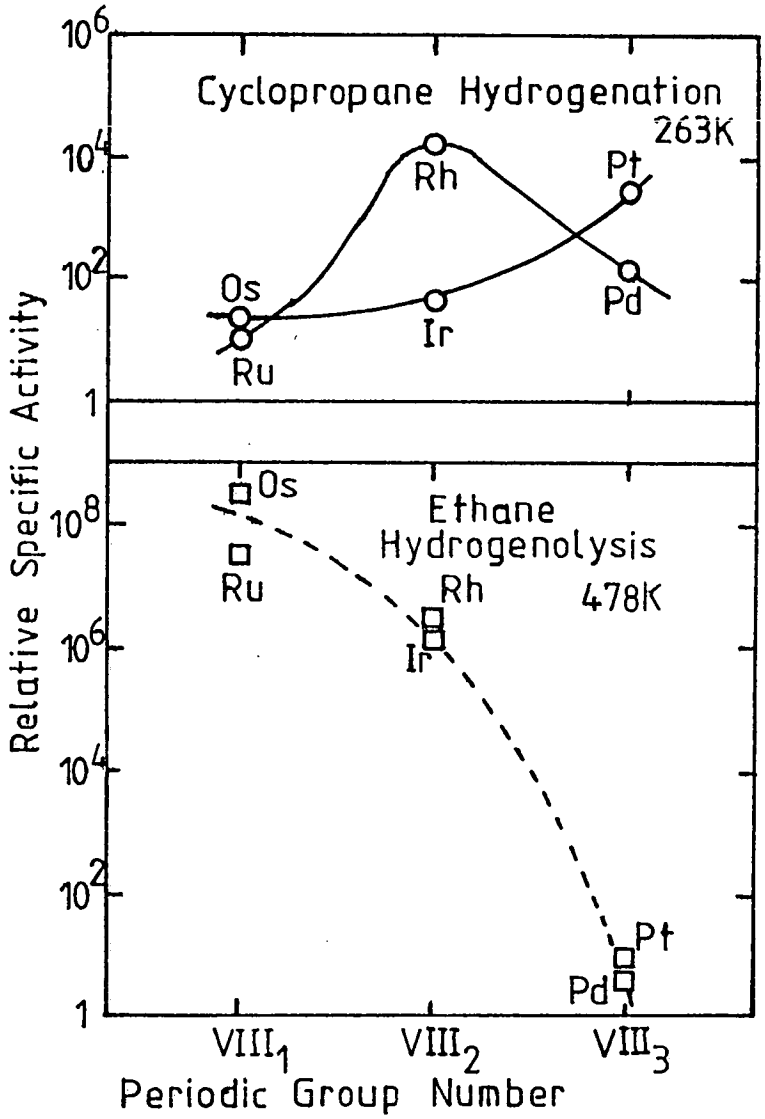

Figure 1.2 Comparison of activity patterns of the group VIII nobel metals for cyclopropane hydrogenation and ethane hydrogenolysis.

(ii) for the triad of metals comprising ruthenium, rhodium and palladium the catalytic activity for cyclopropane hydrogenation passes through a maximum at Rh, whereas ethane hydrogenolysis activity decreases monotonously from Ru to Pd,

(iii) the cyclopropane hydrogenation reaction occurs much more readily than ethane hydrogenolysis and the range of activities of the metals for the two reactions are quite different, ranging over 10^3 and 10^8 orders of magnitude for the hydrogenation and hydrogenolysis reactions respectively.

Another important aspect of catalysis, the solution of which is even more subtle than that of specificity, is selectivity. This is a measure which relates the relative rates of different surface reactions when the catalyst is modified. Apart from changing the metal modification may also include altering the percentage of metal atoms exposed as previously mentioned. The relative rates of heterogenous reactions taking place in parallel on a catalyst can be used to define how "selective" the catalyst is. Thus if several catalytic reactions are occurring, the selectivity, S, for a chosen product is defined[2] by

$$S = \frac{\varepsilon_i}{\sum_i \varepsilon_i}$$

where ε is the extent of reaction.

By limiting studies to group VIII metals Boudart[5] was

able to discern some patterns of behaviour on the factors which influenced selectivity and specificity of metal catalysts. He took for his examples reactions involving hydrogen and one other molecule and surveyed the experimental results in which the effects of surface structure, change of metal and alloying on the catalytic behaviour were observed. The change of surface structure was brought about either by altering the particle sizes of supported metal catalysts or by varying the crystallographic planes exposed by single-crystal surfaces. Alloying was carried out with group IB metals (usually Cu or Au) which are catalytically inert. The qualitative answers for the three questions he posed, i.e. how large are effects of structure, or metallic nature, or alloying on catalytic activity, are shown in table 1.2.

Table 1.2

Effects of Metal Structure, Nature of the Metal, and Alloying on Activity for Catalytic Reactions

Reaction	Effect of structure	Specificity	Effect of alloying
$H_2+D_2 \rightarrow 2HD$	VS	M	S
$C_2H_4+H_2 \rightarrow C_2H_6$	VS	M	S
cyclo-$C_3H_6+H_2 \rightarrow C_3H_8$	VS	M	S
$C_6H_6+3H_2 \leftrightarrows C_6H_{12}$	VS	M	S
$C_2H_6+H_2 \rightarrow 2CH_4$	S	VL	L
$N_2+3H_2 \leftrightarrows 2NH_3$	S	L	?

Scale: 1 VS 10 S 10^2 M 10^4 L 10^6 VL UP

From ref. 5

The results for the reactions (1)-(4) in table 1.2 indicated much the same pattern of behaviour on the various metals. As the table shows there was hardly any effect of surface structure (less than 10-fold), a small effect of alloying (10-100 fold) and a moderate effect of changing from one metal to another. This class of reaction, which is independent of surface structure, has been called "facile" or "structure insensitive". Reactions (5) and (6), however, are remarkably sensitive to all three variables. The hydrogenolysis of ethane, which was discussed earlier, for example, is slightly dependent on the metal particle size (10-100 fold) but enormously dependent on the nature of the metal (~ 10^8 fold between Os and Pt). Alloying also has a considerable effect, 6 per cent of copper added to nickel reduces the activity a thousand-fold. Ammonia synthesis and decomposition also varies greatly from metal to metal, and there is some effect of particle size. Reactions with these properties have been given the terms "demanding" or "structure sensitive".

The relationship between catalytic activity for a given reaction and the position of a metal in the periodic table is of fundamental interest. Such a relationship introduces a degree of order into catalysis and is useful for obtaining a more complete understanding of the factors influencing catalytic activity. Since the heat of adsorption of a gas on a metal surface is also related to

the position of the metal in the periodic table, inferences can be drawn about the relation between catalytic activity and the strength of the chemisorption bond. Qualitatively we can see that two limiting situations may arise. If the chemisorption is 'weak' the surface coverage will be very small and correspondingly the catalytic activity will be low. Since an increase in a low heat of adsorption increases the uptake, activity will increase in this region with strength of adsorption. At the other extreme of 'strong' adsorption, the surface will be essentially fully covered. However, the surface species may then be so stable that it is difficult to decompose it, again catalytic activity will be small. In this case a decrease in strength of adsorption will lead to increased catalytic activity.

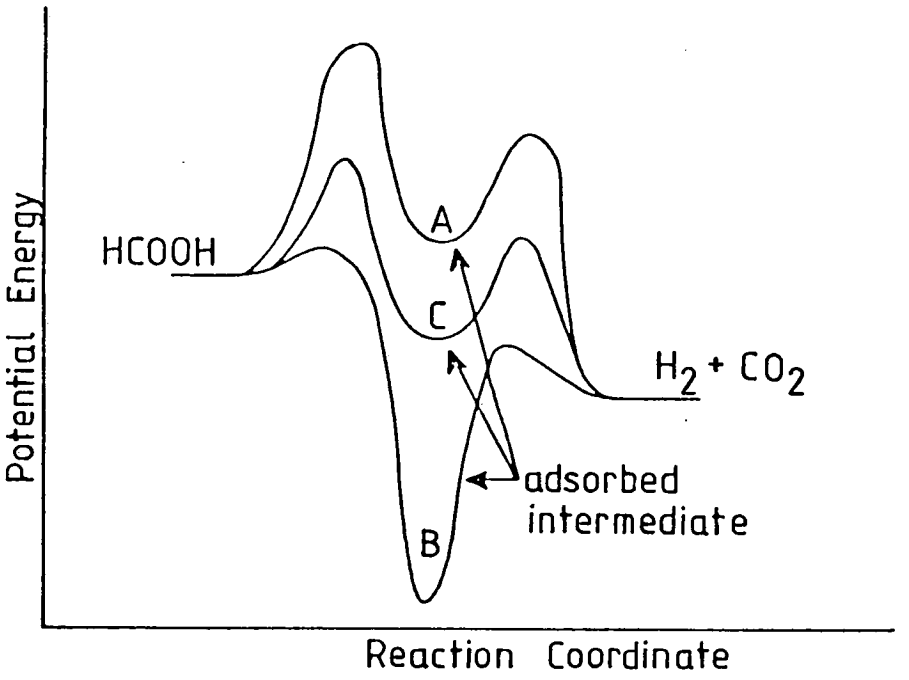

Figure 1.3 Reaction paths for the decomposition of formic acid: formate species - (A) weakly adsorbed, (B) strongly adsorbed, and (C) adsorbed with intermediate strength.

This is shown pictorially in figure 1.3 for the decomposition of formic acid on metals to give hydrogen and carbon monoxide. The interaction between formic acid and metal catalysts is sufficiently strong that a surface compound is formed namely the metal formate[6]. The top curve in figure 1.3 represents the situation when a weakly adsorbed intermediate occurs (A); intermediate (A) is of a rather high energy and is unstable with respect to the reactants. The bottom curve corresponds to the case where adsorption of intermediates (B) was too strong forming a stable intermediate which would require a substantial amount of energy to decompose it. The ideal situation where an intermediate (C) is formed which does not require substantial energies of activation in its formation or decomposition is represented by the middle curve. By measuring the relative activity of a series of metals for the decomposition of formic acid and plotting the temperature required to achieve a fixed catalytic activity against the heat of formation of bulk metal formate, a typical volcano-shaped curve[6] is found, figure 1.4. This shows that for gold and silver the formation of the intermediate is rate determining (the top curve in figure 1.3); and for nickel, cobalt and iron the decomposition of the formate intermediate is rate determining (the bottom curve in figure 1.3).

Another important example illustrating the importance of strength of adsorption is the variation of activity of

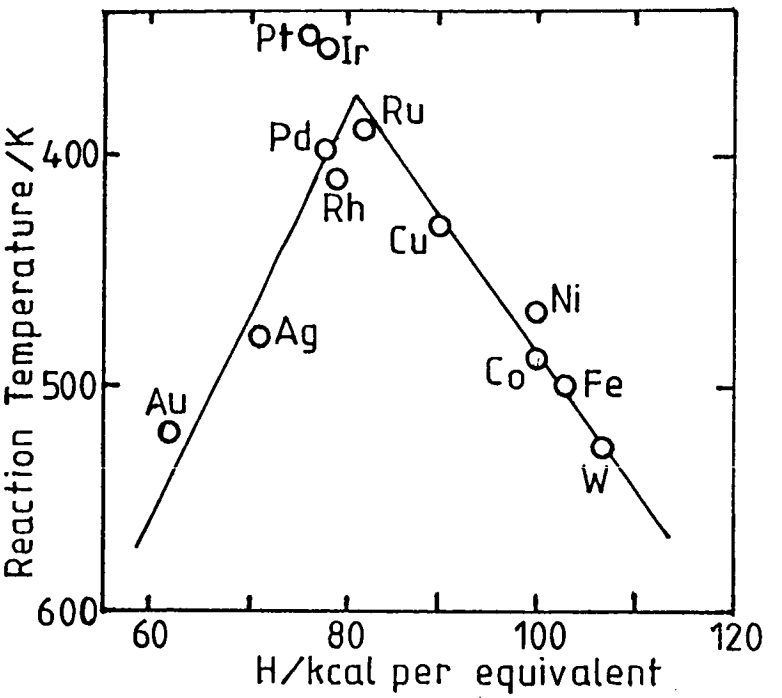

Figure 1.4 The volcano-shaped curve correlating the activity of metals for formic acid decomposition with the heat of formation of bulk metal formates.

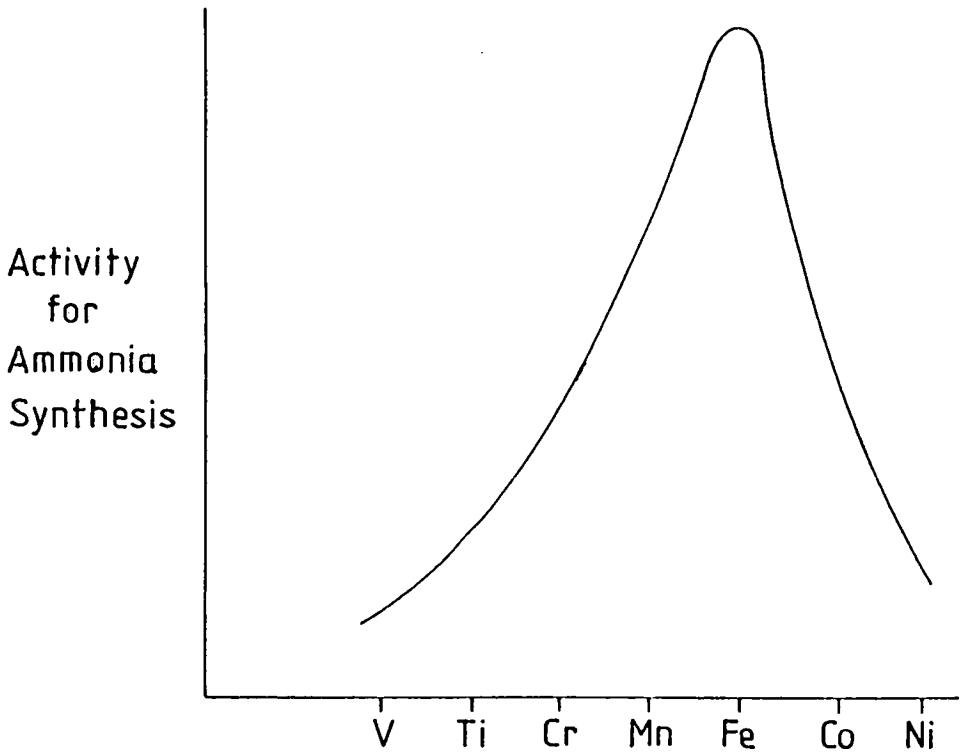

Figure 1.5 Rate of ammonia synthesis variation across the first row of transition metals.

the first row of transition metals for the synthesis of ammonia - shown in figure 1.5. Metals to the left react too strongly with nitrogen, those to the right too weakly and the appropriate strength of adsorption is found with iron which is widely used as an ammonia synthesis catalyst.

1.3 PRINCIPLES OF APPLICATION OF SUPPORTED-METAL CATALYSTS

Since the late 1950's much has been learned about the nature of supported-metal catalysts. In this type of catalyst small metal clusters or crystallites are dispersed throughout porous granules of a refractory material such as silica or alumina[7,8]. The primary particles of silica or of alumina are roughly 15 nm in diameter and are agglomerated into a structure that has the texture of a cemented loose gravel bed. Specific surface areas of the supports are usually in the range 100-500 m^2g^{-1} and the average pore diameters 2.5-15 nm. For a small laboratory reactor the granules would typically be about 0.5 mm in size. For a large industrial reactor the granules would be replaced by uniformly shaped pellets which are somewhat larger perhaps 2-3 mm in size. The model clusters or crystallites in these catalysts are distributed in the pore space of the support, and in some cases the metal clusters are as small as 1 nm in size.

During a catalytic reaction with such catalysts, a

fluid phase (which is often a gas) is passed through a bed of catalyst granules or pellets[7,8] and if the metal particles in the centre of the granule are to be effective as those near the surface concentration gradients must be small. Furthermore, temperature gradients must exist if heat is to flow in or out of the granules accordingly as the catalysed reaction is endothermic or exothermic. If reactions are rapid, serious mass and temperature gradients can occur. The reactant molecules are chemisorbed on the catalytically active metal clusters where a reaction occurs and the product molecule(s) are desorbed into the pores from where they diffuse back into the gas stream. The composition of the gas stream changes as it is depleted of reactant and enriched in product in its passage through the catalyst bed.

Why then does one want to use catalyst granules where problems of mass and temperature gradients may occur rather than the metal particles without a support? Firstly, even at room temperature, the clean metal particles as a powder would undergo some sintering with loss of surface area. Exposure to higher temperatures would aggravate the loss of metal particle area in the powder. However, in the supported catalyst, the location of the metal particles greatly inhibits their 'getting together' and fusing with consequent loss in area even at temperatures in excess of 773K. Thus, carbonaceous deposits which accumulate on the catalyst during reactions

involving hydrocarbons can be removed by treatment in oxygen. Secondly, metal can be used efficiently, since it is easy to make supported catalysts in which over half of the metal atoms are on the surfaces of the metal particles, i.e. particles smaller than 2 nm. Finally, if one used the metal powder in a fixed bed reactor (for example a vertical tube containing a bed of catalyst through which the reactant gases flow) attainment of any reasonable flow rate through a bed of such small particles would result in an enormous pressure drop, whereas, in the case of catalyst granules of some millimetres diameter, the pressure drop is not so large as to cause any problems.

1.4 SUPPORT INTERACTIONS

The role of the support as an inert carrier of the active metal is rather a simplistic view. As well as controlling the average size distribution and location of the metal particles the support itself may play a direct role in the catalytic reaction, i.e. the total catalyst consisting of metal plus support may be bifunctional. The best known examples of such a phenomenon are reforming catalysts such as platinum supported on alumina or platinum supported on a zeolite in which the acidic support functions as the seat of carbonium ion isomerisation activity, while the platinum provides a hydrogenation/dehydrogenation function.

It was realised, however, that the support should in some way exert some influence on the metal. The first deliberate attempts to explore metal-support interactions and to manipulate them were made by Schwab[9] and Solymosi[10] in the 1960's who showed that changing the semiconducting properties of the support by altervalent ion doping affected the activation energies of a number of reactions. More recently from research originating at Exxon a series of publications, starting in 1978[11], demonstrated that transition metal cations (titanium cations in particular) could interact strongly with adjacent metal atoms. This prompted an investigation of titania-supported group VIII metals and led to the discovery of the highly unusual chemisorptive properties of these systems and to the designation of "strong metal-support interaction (SMSI)". The large amount of research since then on metal-titania and related systems has provided clear evidence of strong interactions between transition metal oxide surfaces and supported metals[12,13].

As well as these two types of metal-support interactions other forms of support effects may be envisaged, as discussed by Boudart and Djega-Mariadassou[14]. For example by interacting with the metal the support may induce structural changes of the metal particles, raft-like morphologies have been observed on alumina and titania treated at high temperatures[15,16,17,18]. Different supports may also

favour the formation of particles of different sizes[17,19]. Such changes in particle size and shape can cause shifts in catalytic activity or selectivity by changing the concentration of edge or corner sites, modifying the intrinsic electronic properties of the metal crystallite favouring the presence of a particular crystal face, or altering the number of ensembles of a given size.

The reducibility of a metal may also be strongly influenced by interactions with an oxide support. Silica supported nickel is an extreme example of this, where the reduction of the supported catalyst is much more difficult than that of the bulk nickel oxide. This phenomenon has been suggested to be due to the formation of NiSi alloys at high temperatures[20].

1.5 STRONG METAL-SUPPORT INTERACTIONS (SMSI)

The results of the large amount of study of strong metal-support interactions are now well established - after a reduction at high temperature, usually taken to be 773K, group VIII metals supported on reducible oxides such as TiO_2 undergo drastic reduction in their ability to chemisorb H_2 and CO. Group VIII metals normally chemisorb hydrogen and carbon monoxide at room temperature with a stoichiometry of approximately one H atom or CO molecule per surface metal atom; the extent of chemisorption on a catalyst can thus be used as a measure of metal dispersion, and hence particle size. The inability of the

group VIII metal supported on a reducible oxide to chemisorb H_2 or CO after reduction at 773K cannot be attributed to sintering[11]. The possibility of encapsulation of the metal particles due to extensive restructuring of the support was also discounted because the BET surface area of the sample was not affected by the high temperature treatment in hydrogen. Further studies revealed that this suppression of H_2 and CO adsorption could be reversed by treatment in oxidising atmospheres for most group VIII metals. Oxidation at 623K followed by reduction at 473K has been found to partially restore the chemisorptive properties of titania-supported nickel[21], platinum[22,23], palladium[11] and rhodium[24,25,26] catalysts. It has also been reported that exposure to water leads to a partial reversal of strong metal-support interactions in Rh/TiO_2[27] and Pt/TiO_2[18,27].

Despite extensive studies of systems exhibiting strong metal-support interactions the exact nature of the interactions initiated by high temperature reduction is still controversial. The models proposed for the origin of SMSI can be grouped into four categories: electron transfer, morphological effects, alloying and decoration.

It has been suggested that an electronic interaction between the metal particles and a partially reduced support is involved. In the case of titania supported metals the metal particles are believed to interact with titanium cations with electron transfer to the metal

resulting in the suppression of H_2 and CO chemisorption[28]. It has also been demonstrated that changes in the metal structure occur on reduction of Pt/TiO_2 at high temperature[17]. The formation of overlayers of a partially reduced titanium dioxide, TiO_x, on the surface of the metal crystallites after high temperature reduction has also been suggested[29,30]. The migration of titanium species onto the surface of TiO_2-supported metal particles results not only in partial blocking of the metal surface, but also in the modification of the electronic properties of neighbouring surface metal atoms. Thus the suppression of chemisorption may be attributed to both geometric and electronic effects produced by the migration of these reduced species of the support.

In their original work Tauster *et al*[11] estimated that formation of the intermetallic compound was thermodynamically possible under their high temperature reducing conditions. Since then studies have shown that this intermetallic compound does have a lower H_2 and CO uptake than pure Pt but although the formation of the intermetallic compound was thermodynamically possible it was ruled out for kinetic reasons. Another model which has been proposed to explain the suppression of H_2 and CO chemisorption after high temperature reduction is that after this pretreatment strongly chemisorbed hydrogen remains on the surface rendering a fraction of the metal surface atoms inaccessible to further adsorption at room

temperature[31]. Of these models the electron transfer and decoration models have been the most actively considered.

The creation of anion vacancies in the surface of TiO_2 is believed to be an essential first step in the development of strong metal-support interactions[11,32]. TiO_2 is known to be reducible, and will lose some O_2 even during heating in vacuum. Reduction in H_2 is fairly slow at low temperatures but has been shown to be catalysed by the supported metal[33]. From e.s.r. measurements, Huizinga and Prins[34] found that after reduction at 573K a Pt/TiO_2 catalyst contained 0.3% Ti^{3+} ions. It is thought that after a high temperature reduction the TiO_2 support has a very highly mobile surface with surface and bulk anion vacancies, OH^- ions and Ti^{3+} ions, in a dynamic and very fluid equilibrium. If the surface of TiO_2 exposes Ti^{3+} ions a transfer of electrons between Ti^{3+} ions and adjacent metal atoms becomes possible, but as yet no conclusive evidence exists for significant transfer of charge from the reduced titania to group VIII metal particles. This electron transfer model however does not fully explain strong metal-support interactions. For example, strong metal-support interactions are observed for both very small ($\leqslant$ 2 nm) and large (> 10 nm) particles[19,21,35,36], and while it is possible to understand interactions between the support and highly dispersed metal species, it is hard to imagine how the localised interactions of electron transfer between the

titania support and large metal particles at the metal-support interface would affect the chemisorptive and catalytic properties of the larger metal particles. Also, as it has been estimated that the electronic perturbations in the metal would be negligible beyond a distance of about 0.5 nm from the metal-support interface[37], this fact raises the question whether the extent of charge transfer is large enough to affect the properties of the metal.

Although the degree to which charge transfer occurs and the effect upon the properties of the metal is as yet not fully understood, the interaction of Ti^{3+} ions with metal atoms is thought to be related to the driving force for the migration of reduced titania species from the titania support onto the metal surfaces[29,36,38,39]. This has been termed the "decoration model"[38], the evidence for which has been highlighted by both conventional catalytic studies[29,30,36,38,40] and surface science techniques[41-45]. Thus, at present, it is envisaged that during catalyst preparation small amounts of titania species may dissolve into the impregnation solution and be deposited onto the surface of the metal particles[29]. This titania as well as titania at the metal-support interface, will be reduced during pretreatment in hydrogen, at a certain temperature reduced titania moieties become mobile and spread over the metal particle surface. The driving force for this migration is the chemical interaction that takes place between reduced titania species and surface metal atoms;

this is the same driving force responsible for the spreading of metal particles over titania surfaces[17,18]. The adsorption of carbon monoxide and hydrogen would then be suppressed as adsorption sites are blocked.

1.6 INFLUENCE OF STRONG METAL-SUPPORT INTERACTIONS ON THE CATALYTIC PROPERTIES OF TITANIA-SUPPORTED METALS

Soon after the discovery that high temperature reduction could alter the chemisorptive properties of group VIII metals supported on reducible oxides it was found that catalysts of this type could also exhibit unusual catalytic properties. As previously mentioned in section 1.1, catalytic reactions can be classified into structure-insensitive (hydrogenation, dehydrogenation, isomerisation, hydrogen exchange) or structure sensitive (hydrogenolysis, carbon monoxide hydrogenation and ammonia synthesis) reactions depending on the extent to which the rate of reaction and its selectivity are affected by the size and morphology of the metal particles.

As expected, structure insensitive reactions were least affected by SMSI. For example, the activities of Rh/TiO_2 and Pt/TiO_2 catalysts for benzene hydrogenation were decreased by only one order of magnitude[39,46], and the rates of ethene hydrogenation over Pt, Ir, and Rh

supported on titania were also only slightly affected by the high temperature reduction[47]. In general the hydrogenation of unsaturated alkenic and aromatic carbon bonds are typically suppressed by a factor of 5-10 (on a per gram of metal basis) after a high temperature reduction. Strong metal-support interactions in Ni/TiO_2 and Rh/TiO_2 catalysts also favour the dehydrogenation of cyclohexane to benzene[38,48-50], and the reduction of titania-supported platinum and nickel at 773K was found to decrease the rate of isotopic exchange of cyclopentane with deuterium during illumination[51]. This reaction has also been shown to be slightly suppressed over Rh/TiO_2 after a high temperature reduction[52]. As for hydrogen and carbon monoxide chemisorption, the activities of the catalysts for these reactions could be partially or fully restored to their initial activities by an oxidation treatment followed by a low temperature reduction.

The reactions for which titania-supported catalysts have been shown to have unusual activities after a high temperature reduction are the hydrogenolysis of alkanes and the hydrogenation of carbon monoxide. The former reaction which involves the breaking of C-C bonds is severely suppressed, factors of up to 10^4 being reported for ethane hydrogenolysis over several TiO_2-supported metal catalysts[53] and a similar amount for butane hydrogenolysis over Ir/TiO_2[54] and Rh/TiO_2[55]. On the other hand, the activity of titania-supported metals for carbon

monoxide hydrogenation is enhanced. This was first reported in a paper by Vannice and Garten[56] in which they obtained, on a per-gram nickel basis, an order of magnitude greater activity for Ni/TiO_2 than Ni/Al_2O_3, Ni/SiO_2, and Ni/graphite. They also reported a shift in selectivity towards higher hydrocarbons with the Ni/TiO_2 system.

The loss of hydrogenolysis activity for TiO_2-supported catalysts may arise for the same reasons as postulated for the reduction in chemisorption ability after a high temperature reduction, the dominant effect varying from one metal to another. Possible effects are; loss of metal surface area due to migration of the particles into the support; the elimination of small, highly active particles; a change in the morphology of the metal particles; or electronic interactions with the support. Although there is little information available it has been found that the activation energy for hydrogenolysis remains the same but the pre-exponential factor changes[49,50,57,58,59]. This would suggest that it is the number rather than the nature of the active sites which is principally affected by the high temperature reduction. The hydrogenolysis activity of these catalysts decreases with increasing reduction temperature[40,47,49,50,55,60-62] but oxidation followed by re-reduction at a low temperature[60-62] restores some or all of the original activity. Activities measured after a low temperature

reduction of about 473K are reported to be similar to those measured for silica- and alumina-supported catalysts.

Since the benefits of titania-supported group VIII metals as catalysts for CO hydrogenation had been demonstrated[54], this reaction has been extensively used as a probe to investigate metal-support effects and rate enhancements have been observed over many, but not all, group VIII metals supported on titania[63-71]. More recently a study of acetone hydrogenation over platinum supported on several oxides, including TiO_2, has shown that this reaction is also enhanced by a high temperature reduction[72]. The authors suggested that the metal-support effect which enhances CO hydrogenation is a more general phenomenon and has the potential to increase rates of hydrogenation of other carbonyl bonds. The mechanism by which the activity of the titania-supported catalyst is increased is thought to be the same as that proposed for CO hydrogenation.

It is believed that modification of the number or type of active sites are responsible for these unusual properties of titania-supported catalysts. Indeed it is found that these catalysts have higher activation energies than the alumina-supported metals[66,67]. It has been proposed that the increased activity and selectivity of many supported metals is due to participation of the support in the reaction[60,68,73,75]. In a model

contemplated by Burch and Flambard[60] a new class of active site was proposed to exist at the interface between the support and metal, as shown in figure 1.6. These sites were envisaged to participate in CO hydrogenation by assisting CO dissociation through adsorption of the oxygen-end of the molecule into anion vacancies created by spillover of hydrogen from the metal to the support.

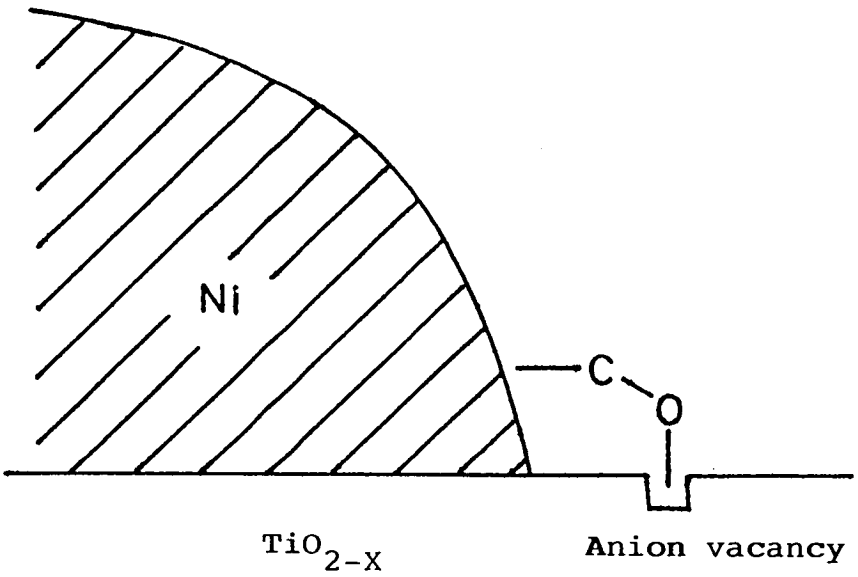

Figure 1.6 Model of Burch and Flambard[60] for interfacial interaction of nickel and titania during CO hydrogenation.

During hydrogenation of acetone the creation of these sites by high temperature reduction increases the concentration of di-σ-bonded intermediates. These are formed by activation of oxygen atoms by the oxygen vacancies on the titania support. The intermediates are

then hydrogenated by atomic hydrogen provided by the available platinum metal to propan-2-ol[72]. Other possibilities for the enhancement of CO hydrogenation on high temperature reduced catalysts include the adsorption of CO on the support which is then hydrogenated by hydrogen spillover from the metal[68], or the reverse spillover of hydrogen from the oxide to the metal, where it may participate in the reaction[76].

1.7 OTHER OXIDE SUPPORTS

Tauster and co-workers also reported on the ability of several transition metal oxides to suppress the CO and H_2 chemisorption capacity of supported iridium[77]. Indeed there was a general correlation between the temperature required to induce a strong metal-support interaction and the reducibility of the oxides. The order of decreasing temperature for the onset of SMSI was reported as

$$ZrO_2 > Ta_2O_5 > V_2O_3 > TiO_2 > Nb_2O_5.$$

Oxide surfaces are known to be more reducible than predicted from bulk thermodynamic data[77], e.g. a report that Pt supported on MgO loses its capacity to adsorb H_2 after a high temperature reduction[78] indicates that suppression of chemisorption may occur also for supports which are essentially irreducible. Another example of an oxide being more reducible than predicted is the finding that lanthana, La_2O_3, in the presence of Pd undergoes surface reduction to LaO_x and gives evidence of

metal-support interaction reminiscent of titania-supported metal catalysts, i.e. suppressed CO chemisorption, altered CO *vs.* H_2 adsorptive competition, and enhanced CO-H_2 synthesis activity[79,80]. These observations raise the possibility that the phenomena associated with strong metal-support interactions may be quite general, extending to main group as well as transition metal cations.

From the previous discussion it is evident that the bulk of the research activity carried out in the investigation of strong metal-support interactions has largely concerned TiO_2, with relatively few studies devoted to the two oxides which exhibited similar properties, i.e. vanadia, V_2O_5, and niobia, Nb_2O_5.

The former has received only scant attention and has raised some controversy. It was originally reported that rhodium on vanadia showed greater activity and selectivity to oxygenates during CO hydrogenation than rhodium on other supports[81] but a more careful study using vanadia as support[82,83] indicated that the difference could be attributed to the method of preparation of the catalysts. As V_2O_3 is soluble in acidic media the pH of the impregnating solution is important and during preparation of the catalysts the use of $Rh(NO_3)_3$ or $RhCl_3$ causes the dissolution of some V_2O_3 as vanadyl complexes which precipitate on drying[84,85] so that reduction gives metal particles embedded in a poorly defined and perhaps amorphous environment. Nevertheless, it was

concluded[83,86] that hydrogen spillover occurred to a greater extent on V_2O_3-supported catalysts than on TiO_2-supported samples, and that the chemical interaction between V_2O_3 and the supported metal is different from that between TiO_2 and the supported metal.

Niobia-supported metals have received more attention, as well as niobia-promoted silica catalysts. It was shown by Ko *et al*[87] that when niobia was used as a support for Ni the suppression of adsorption capacity after a high temperature reduction for H_2 and CO was greater than reported for titania. It was also found to produce, unlike other nickel catalysts, significant quantities of alkenes during CO hydrogenation and at a rate which was also increased after a high temperature reduction[88]. The stronger suppression of H_2 and CO chemisorption was explained by the greater reducibility of niobia[77,89]. The rate of ethane hydrogenolysis over Ni/Nb_2O_5 was also greatly reduced by high temperature treatment - again typical of an 'SMSI' catalyst. Niobia-promoted silica catalysts also exhibit 'SMSI' features[90,91], as strong as that in the niobia-supported rhodium catalyst. Decoration of the metallic surface with reduced niobia species (NbO_x) was suggested for the latter results. More recently addition of deuterium to ethene over Ir/Nb_2O_5 and Rh/Nb_2O_5 has indicated that two different environments exist after a high temperature reduction, i.e. at the bare metal surface and at the metal/NbO_x interface[92]. In these two

environments the hydrogen isotope ratio was believed to be different leading to dissimilar deuterium distributions in the resulting ethane.

1.8 CONCLUSIONS

At the present time the best explanation of the existence of strong metal-support interactions (SMSI) seems to be the decoration model, i.e. the presence of a sub-oxide species of the support (TiO_x, NbO_x, LaO_x, etc.) on the metal surface.

Metal/titania systems exhibit normal chemisorptive properties after a low temperature reduction (LTR). A high temperature reduction (HTR) typically causes suppression of the amount of H_2 or CO adsorbed. Hydrogenolysis activity is similarly affected by HTR, while the effects on reactions involving C-H bonds are less pronounced. In contrast to these results metal/titania and related catalysts exhibit higher activity for CO hydrogenation (as shown more recently for $(CH_3)_2CO$ hydrogenation) than their silica- or alumina-supported counterparts. Although much of the evidence suggests that the presence of TiO_x species on the metal surface is responsible for these unusual properties, the exact manner by which these sub-oxide species alter the chemisorptive and catalytic properties of the metal is still not fully understood. However, some of the results obtained indicate an electronic effect, it is therefore

possible that some degree of electronic modification of the metal atoms occurs at the metal-support interface. This situation is, of course, further complicated by the fact that if TiO_x migrates onto a metal particle this creates a new 'interface' which may make an important contribution to the changes in the overall catalytic properties.

The dramatic changes observed in metal/titania and related systems following an HTR have tended to overshadow the smaller but nevertheless significant differences in catalytic properties between metals supported on reducible oxides and their silica- or alumina-supported counterparts. There is evidence in the literature that titania-supported metals after a LTR where they have normal adsorption properties may have unusual catalytic properties. For example, it has been well established that normal titania-supported metals have a higher activity for the CO/H_2 reaction[60,68]. Recently, it has been shown that Rh/TiO_2 catalysts have a high activity for n-hexane conversion[93,94] and give quite different product distributions in the n-hexane[94] and methylcyclopentane[93] reactions. It has also been demonstrated that Pt/TiO_2 catalysts give quite different product distributions to Pt/SiO_2 catalysts for both methylcyclopentane[58] and n-hexane[59] reactions.

Results for supported Rh catalysts had shown that (a) similar activities were obtained for silica- and

niobia-supported samples following a mild reduction[90,91] and (b) the activity for ethane hydrogenolysis over the latter was severely suppressed after an HTR. Carbon monoxide hydrogenation over Rh/Nb_2O_5 reduced at 573K was nearly two orders of magnitude more active than similar alumina- and silica-supported samples and also showed a higher activity for C_2-C_5 hydrocarbons[95]. Infra-red studies indicated that CO dissociation was more rapid over Rh/Nb_2O_5 than over the alumina-supported sample.

Clearly niobia as a support required further investigation, both for hydrogenolysis and carbon monoxide hydrogenation. It has also been demonstrated[57,58,94] that when supported on titania platinum enters the SMSI state much more readily than rhodium and is consequently less able to recover its original adsorption capacity. Thus niobia-supported platinum and rhodium warranted further investigation and their hydrogenolytic activities seemed a potentially fruitful area of research.

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CHAPTER 2

APPLICATION OF DEUTERIUM NMR IN THE STUDY OF HYDROCARBON EXCHANGE REACTIONS

2.1 INTRODUCTION

It is well understood that the study of exchange reactions can provide important information about the nature of intermediates formed on the surfaces of catalysts. The replacement of hydrogen atoms in hydrocarbons with deuterium can be readily determined using a mass spectrometer and this provides the isotopic distribution in the hydrocarbon d_i (where d_0, d_1, d_2 ....., is the percentage of products containing no D atoms, one D atom, two D atoms, etc.). The pattern of these products in the initial stages of a reaction is determined by the nature of the adsorbed intermediates and by their reactivity. Although such studies have provided much information on the types of intermediates formed on a wide range of catalysts, the determination of d_i from parent molecule ions in the mass spectrometer provides no direct information about the location of deuterium in the exchanged molecules. Further information can be obtained by using hydrocarbon molecules which due to symmetry considerations predetermines the types of intermediate formed, e.g. if d_5 is a large maximum in exchanged cyclopentane, then one can reasonably assume that the five deuterium atoms in $C_5H_5D_5$ are those on the same side of

the ring and attached to different carbon atoms.

Other physical techniques that have been used in determining the location of deuterium in exchanged molecules are the spectroscopic techniques of infra-red, microwave and nuclear magnetic resonance. As indicated by Burwell[1] location of deuterium atoms by infra-red can only be achieved in special cases, e.g. Patterson and Burwell[2] were able to measure the amount of exchange into the hydroxyl groups of alcohols. This type of analysis is notoriously difficult by mass spectrometry as the exchanged hydroxyl group undergoes further exchange on the metal walls of the instrument. Microwave spectroscopy[3] has been used successfully to locate exchanged deuterium in propene and but-1-ene but the technique is only applicable to molecules containing a dipole moment and is therefore limited in its application. The most extensively used method has been nuclear magnetic resonance, nmr, although this also is not without its limitations. The location of the deuterium atoms are deduced from the subtraction of a proton nuclear magnetic resonance spectrum of an undeuterated reference sample from the spectrum of a deuterated sample. The method therefore requires the protons in different positions to be well resolved, allowing the technique to be applicable only to alkenes and to cycloalkanes where restrictions on confirmation may permit the separation of protons.

In his review Burwell[1] mentions that it would be

preferable to measure the gain in a deuteron signal but at that time, 1972, the facilities required to do this were not commonplace. However, by the end of that decade the high resolution, high field instruments required to measure the very weak deuteron signal were more widely available and the experiments Burwell had envisaged are now possible.

It would be beyond the scope of this chapter to review all the preceding work which has been done in determining the mechanistic details of exchange reactions over heterogeneous catalysts. However, in order that a better appreciation of the role deuterium nuclear magnetic resonance has played in extending our understanding about exchange mechanisms over oxide and metal catalysts it is desirable to briefly describe what the current ideas of mechanisms are.

2.2 EXCHANGE OF HYDROCARBONS WITH DEUTERIUM

Over the years since 1951 a large number of studies of hydrocarbon exchange reactions with deuterium over metal and oxide catalysts have been reported and a number of reviews have been published [1,4-10]. The main features of exchange processes were first recognised and analysed by Kemball[4]. The simplest hydrocarbon to be exchanged with deuterium was methane, and this also proves to be the most difficult[11,12]. Typical initial distributions for methane-deuterium exchange over metal films are shown in

table 2.1. All four isotopically exchanged methanes are initially formed indicating that two exchange mechanisms are operating; a simple stepwise exchange and a multiple exchange process. The intermediate for stepwise exchange

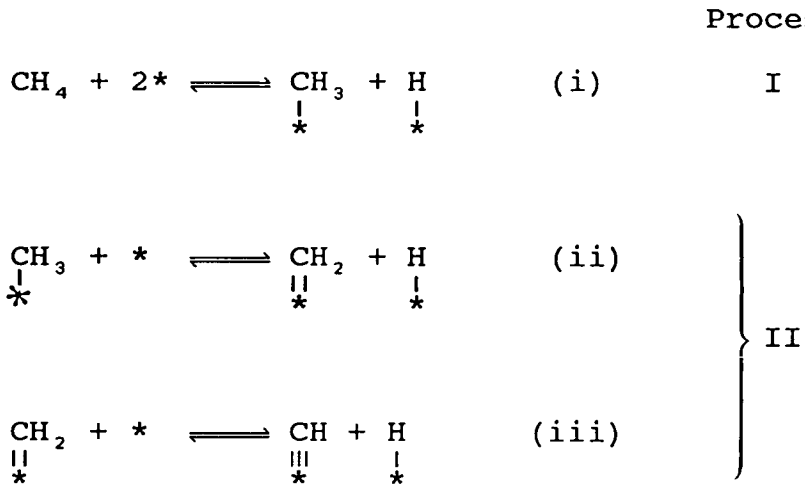
Table 2.1

Initial Product Distributions for Methane Exchange over Evaporated Metal Films

		Initial Production Distribution (%)			
Metal	Temp./K	D_1	D_2	D_3	D_4
Rh	435	21	5	29	45
Ni	510	12	3	24	26
Pt	532	36	12	25	27
Pd	427	95	1	2	2
W	424	76	1	9	14

is believed to be an adsorbed methyl radical formed by dissociation of a methane molecule, and this subsequently combines with a deuterium atom to give the product, CH_3D. The presence of other methane species with a higher deuterium content infers that metal-carbon multiple bonds are being formed. The amounts of CD_4 were typically greater than CD_3H and CD_2H_2 which indicates that the methylene radical once formed undergoes extensive reaction before returning to the gas phase as the fully exchanged methane molecule. The mechanism for methane exchange is

shown in scheme 2.1. Kinetic studies[12] indicated that the



Scheme 2.1 Mechanisms for methane exchange

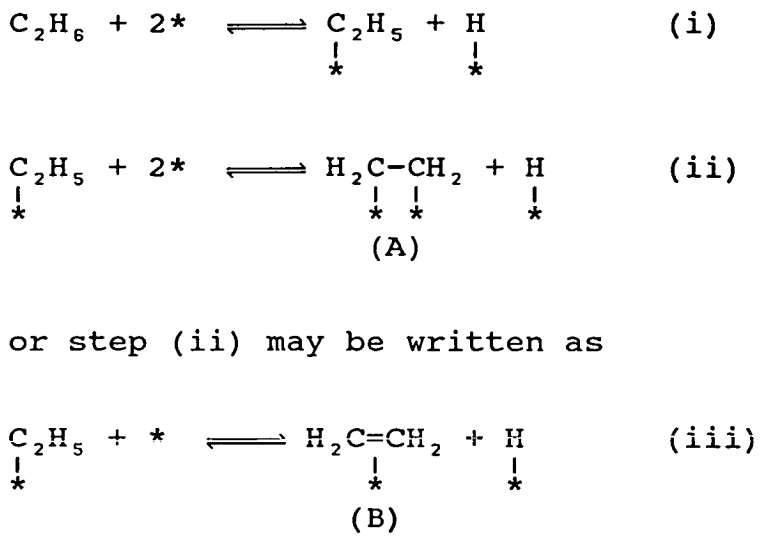
reaction order with respect to deuterium was generally more negative for multiple exchange, process II, than for stepwise exchange, process I, thus process II is more retarded by the presence of deuterium suggesting that further dissociation of the adsorbed methyl radical is required. As the activation energy for multiple exchange is higher than for stepwise exchange further dissociation of the CH_3 intermediate, step (ii), requires more energy than step (i), i.e. the initial formation of the methyl radical. The large amounts of CD_4 formed indicates that once step (ii) takes place it is followed by a rapid and repeated exchange to form a fully exchanged methylene intermediate before recombination with deuterium to reform the methyl radical occurs.

Table 2.2

Initial Product Distribtions for Ethane Exchange over Evaporated Metal Films

Metal	Temp./K	Initial Production Distribution (%)					
		D_1	D_2	D_3	D_4	D_5	D_6
Rh	273	5	3	4	7	17	64
Ni	435	40	10	4	5	10	30
Pt	407	19	17	12	10	16	26
Pd	418	5	6	9	10	19	51
W	219	79	12	5	2	1	1

Table 2.2 shows that ethane exchange with deuterium occurs at lower temperatures than methane over evaporated metal films[13]. The initial product distributions show that the multiple exchange process occurs more readily with ethane over certain metals, e.g. Pd gives a very large amount of C_2D_6 compared to the largely stepwise exchange it exhibited with methane. To account for this the formation of the diadsorbed $\alpha\beta$-species, (A), from a mono-adsorbed ethyl radical, scheme 2.2, must occur more readily than the interconversion of the methyl radical to the $\alpha\alpha$-diadsorbed species of methane. It is not possible to unambiguously identify the intermediate as the $\alpha\beta$-diadsorbed species (A) or the π-complexed species (B) as both produce the same results. Scheme 2.2. indicates

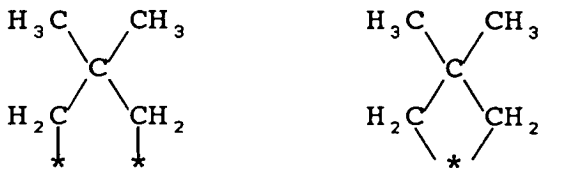


Scheme 2.2 Proposed reaction scheme for ethane exchange

the $\alpha\beta$-process where the intermediate can easily propagate along a chain of carbon atoms, and, in linear alkanes with rapid rotation about the C-C bonds, every hydrogen atom can be readily replaced.

The presence of a quaternary carbon atom in a hydrocarbon has been noted as an obstacle for promoting multiple exchange in hydrocarbons. Many examples of this have been reported in the literature[4,8,14], e.g. with 3,3-dimethylpentane the only maximum of 5 exchanged H atoms observed in the initial stages of reaction corresponded to the molecule $C_2H_5C(CH_3)_2C_2D_5$. In contrast results with 2,2-dimethylpropane show that a single-exchange mechanism always prevails and only at high temperatures does some $\alpha\alpha$-multiple exchange take place. Over Rh a process of exchange is observed which can be

explained only by invoking the existence of an $\alpha\gamma$-diadsorbed intermediate, scheme 2.3.



$\alpha\gamma$-diadsorbed species

Scheme 2.3 **Proposed 1,3-diadsorbed intermediates for the promotion of multiple exchange in 2,2-dimethylpropane**

The exchange of cyclic hydrocarbons with deuterium has received considerable attention. The results with cyclopentane over metal films at low temperatures[15] and over supported metal catalysts at slightly higher temperatures[8] were very similar. With this cyclic molecule rotation is restricted about the carbon-carbon bonds and if the $\alpha\beta$-process was the only operative exchange mechanism then only five of the H atoms on one side of the ring would be exchanged during one sojourn of the molecule on the surface. The results over Pd show, figure 2.1, that this is not the case where up to ten hydrogens are replaced with maxima at $C_5H_5D_5$ and C_5D_{10}. The ratio of these two isomers decreased with increase in temperature which suggests that an additional exchange

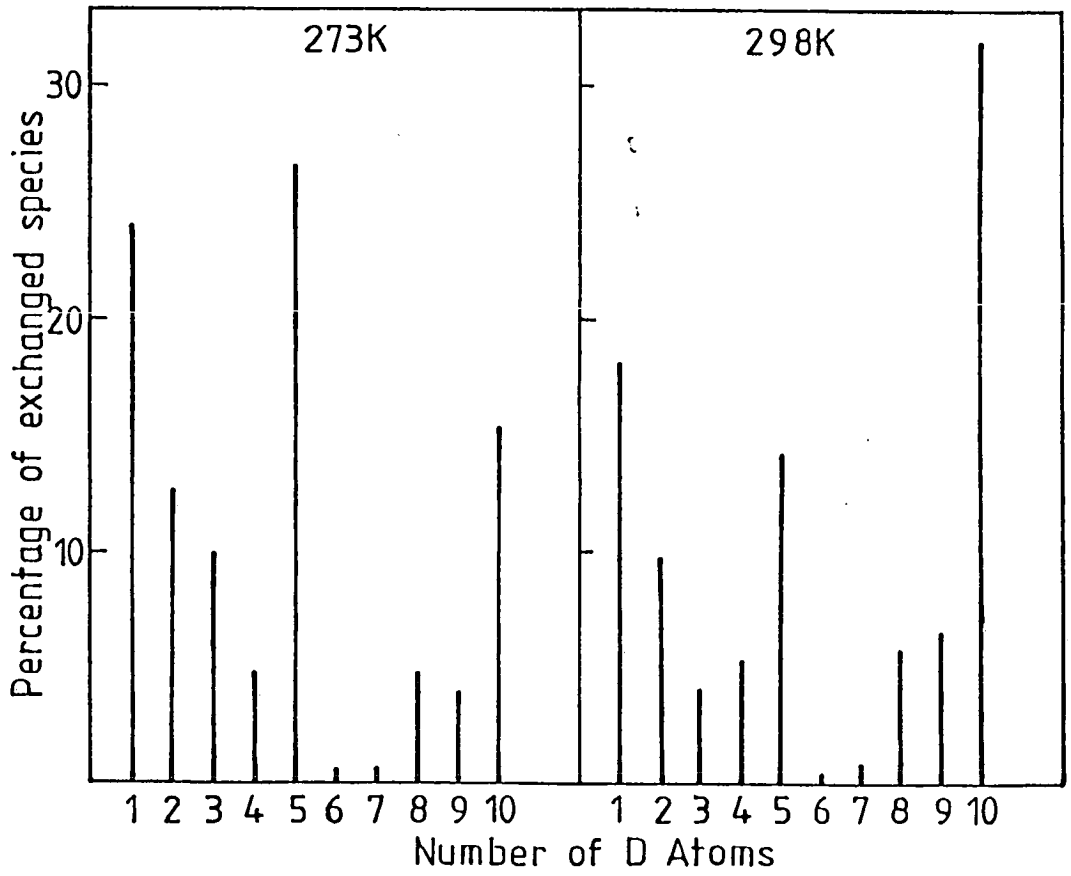
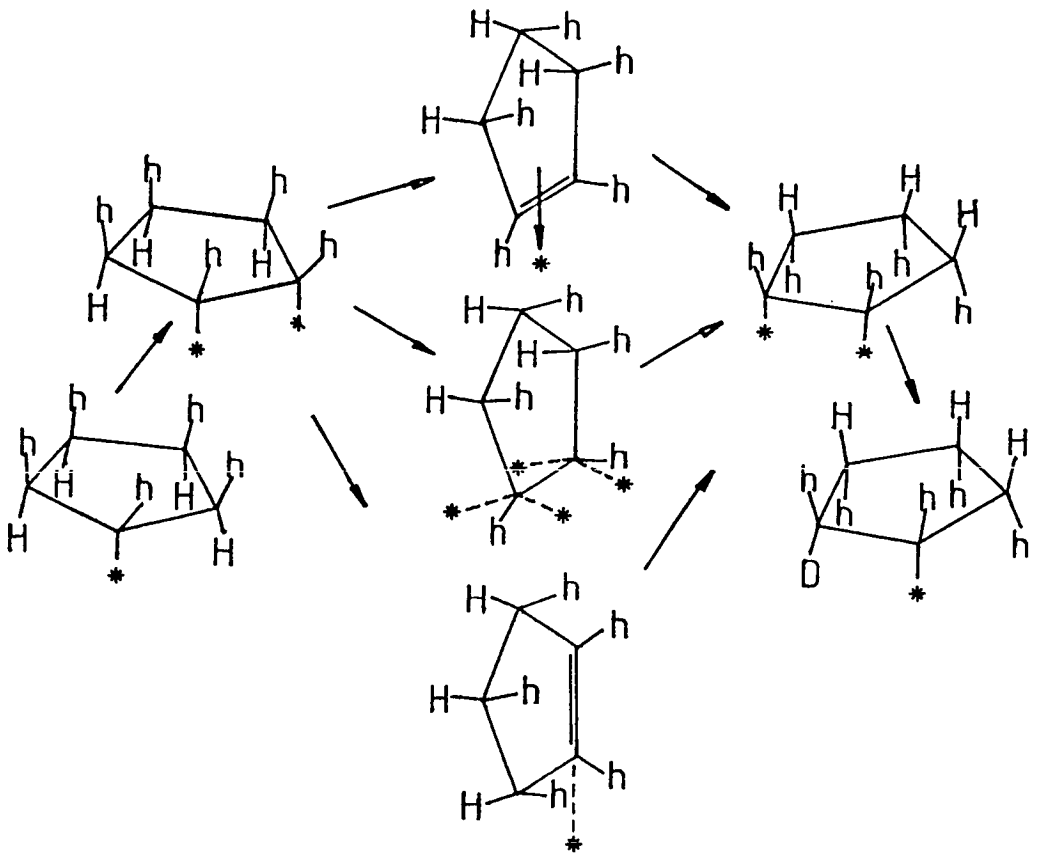


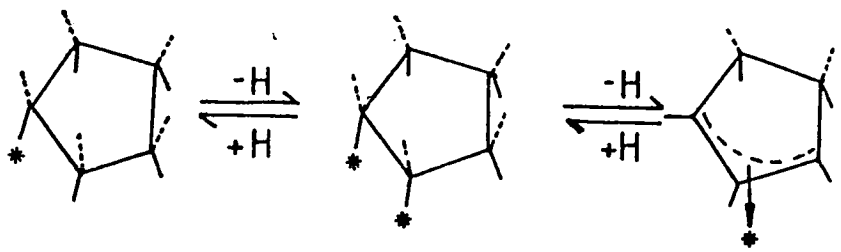
Figure 2.1 Initial product distribution for the exchange of cyclopentane over palladium films

process with a slightly higher activation energy was also taking place.

Two mechanisms have been proposed to account for these data 'roll-over'[8], scheme 2.4 and 'π-allyl', scheme 2.5.

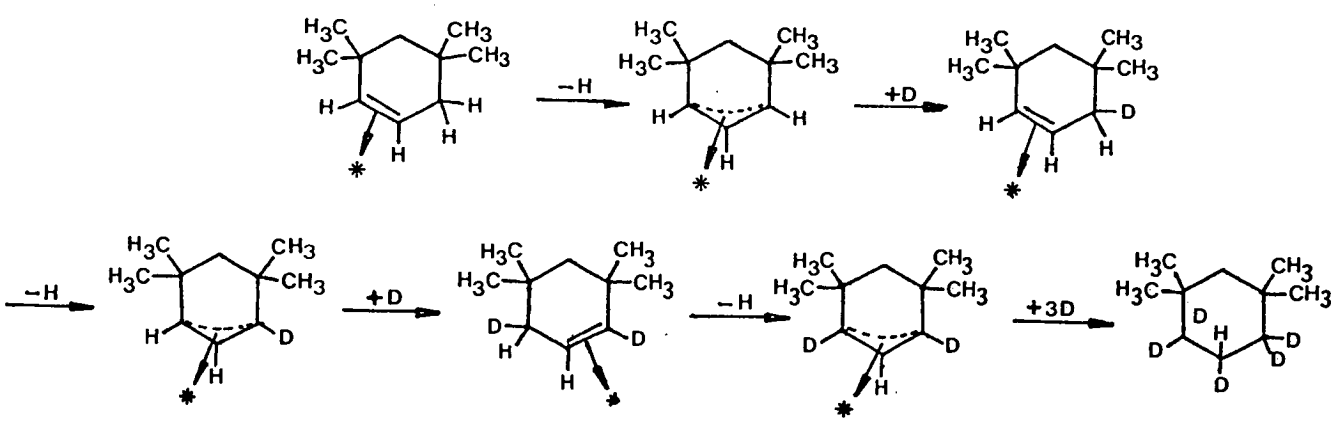


Scheme 2.4 Rollover mechanisms of 1,2-diadsorbed species



Scheme 2.5 The π-allyl mechanism

Rooney[17] suggested that the π-bonded alkene formed from an adsorbed alkyl further interconverts on certain metal atoms, especially on Pd surfaces, with π-allyl intermediates. This would be accompanied by *trans* elimination and addition of hydrogen atoms and would provide an explanation of the initial exchange on both sides of the ring as observed with cyclopentane. To test this theory Rooney investigated the characteristics of the exchange of 1,1,3,3-tetramethylcyclohexane, which has an isolated trimethylene unit, on Pd films[17]. With this molecule interconversion between sp^2- and sp^3-hybridisation is permitted for C_4 and C_6 whereas C_5 must remain sp^2-hybridised. Thus as scheme 2.6 shows there is



Scheme 2.6 The π-allyl mechanism postulated to explain initial exchange of 5 hydrogen atoms in an isolated trimethylene unit.

no mechanism for the ready replacement of the H at C_5 on the side of the ring which is remote from the metal surface. The theory predicts that there should be a maximum concentration of the d_5- and not of the d_6-isomer, and as table 2.3 shows this was indeed the case.

Table 2.3

Initial product Distribution for Exchange of 1,1,3,3-tetramethylcyclohexane over Palladium at 383K

% Isotopic Species									
D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10-20}
28.7	3.9	8.0	14.1	39.2	6.1	-	-	-	-

An alternative mechanism proposed by Burwell[8] postulates the rollover of the $\alpha\beta$-diadsorbed species while still attached to the surface as shown in scheme 2.4. This mechanism explains the absence of easy replacement of a central H atom in an isolated trimethylene unit and also has the advantage of accounting for the small maximum in the d_8 isomer in the exchange of cyclopentane over Pd, see figure 2.1. Thus one rollover of $C_5H_5D_3$ with respect of the $\alpha\beta$-process on certain sites can only give $C_5H_2D_8$. Facile multiple rollover and a rapid $\alpha\beta$-process on other sites will explain the large amount of the d_{10} isomer. This latter mechanism of rollover has now been generally accepted.

As previously mentioned there is still some ambiguity about the nature of the $\alpha\beta$-diadsorbed intermediate whether it is a π-bonded alkene or a di-σ-bonded alkane. From stereochemical considerations of the exchange results for cyclic hydrocarbons[18], $\alpha\beta$-exchange was found to only involve eclipsed *cis*-1,2-diadsorbed alkane. Further evidence that this process is limited to the *cis*-positions in both addition and hydrogen exchange reactions is found in studies of alkene hydrogenation[19]. Burwell also suggested[8] that conversion of certain cyclic compounds to π-bonded alkenes is too endothermic to be acceptable but that these compounds could form the corresponding eclipsed $\alpha\beta$-diadsorbed species without additional strain. However Rooney[14] argued that for the $\alpha\beta$-process to occur the reacting hydrocarbon must have a possibility of forming an alkene complex. He gave as an example the exchange of the caged compound, heptacyclotetradecane, figure 2.2, whose structure contained pairs of CH groups firmly held in an

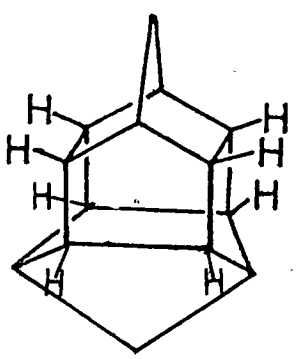


Figure 2.2 Heptacyclotetradecane

eclipsed position and where the formation of a π-bonded intermediate is most unlikely. If the $\alpha\beta$-intermediate only requires eclipsed *cis*-1,2-diadsorption to promote multiple exchange then this molecule would exhibit initial multiple exchange of 2 hydrogens. However, it was reported[20] that the molecule gave only simple stepwise exchange on Pd with the observed distributions of exchanged products agreeing closely with the calculated binomial distribution for a molecule containing 16 exchangeable hydrogens. Therefore as the $\alpha\beta$-diadsorbed species is now known to be a π-complexed alkene Clarke and Rooney[14] suggest that the simplest interpretation of rollover is that the metal-alkene bond breaks: the free alkene has then a transient existence in the gas phase and can migrate from one type of site to another.

2.3 THE APPLICATION OF DEUTERIUM NMR SPECTROSCOPY IN CYCLOPENTANE EXCHANGE

As the foregoing indicates the exchange mechanism of cyclopentane with deuterium is reasonably well understood. Nevertheless there are still some aspects of the exchange process for which there are conflicting interpretations in the literature. Under some conditions it has been found that some metals, usually nickel or rhodium, promote the formation of large amounts of d_2-cyclopentane in their initial products[21-25]. Such observations could be

explained either by the reversible formation of an $\alpha\beta$-diadsorbed species or by $\alpha\alpha$-diadsorbed intermediates. The study of cyclopentane exchange mechanisms by deuterium nmr spectroscopy with its ability to identify specific groupings of deuterium atoms provided a definitive answer.

The potential of deuterium nmr spectroscopy for identifying and estimating the various possible groupings of deuterium atoms in substituted cyclopentanes was ably demonstrated in the investigation of the catalytic reaction of cyclopentene with deuterium on zinc oxide[26]. From a combination of deuterium nmr spectroscopy and mass spectrometric data the authors showed that the exchange of the alkenic hydrogens in cyclopentene occurred without any double bond movement, and the concurrent simple addition of deuterium to the double bond resulted in the formation of d_1- to d_4-cyclopentanes. These reaction products, corresponding to $-CHDCH_2-$, $-CHDCHD-$, $-CD_2CHD-$, and $-CD_2CD_2-$ groupings were readily identified in the deuterium nmr spectrum.

Using a range of metal-supported catalysts, cyclopentane samples containing different amounts of deuterium were generated so that an estimate of isotopic shifts caused by introduction of additional deuterium nuclei into the molecule could be determined[27].

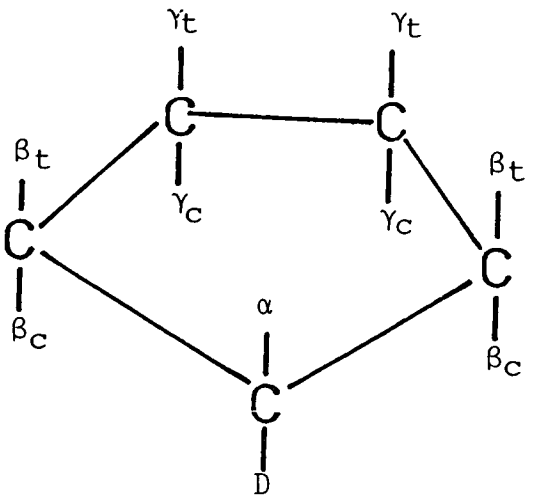


Figure 2.3 Deuterium interactions in a cyclopentane molecule

The possible interactions that a single deuterium in a cyclopentane molecule may undergo with neighbouring deuterium atoms are shown in figure 2.3. The symbols α, β_c, β_t, γ_c, and γ_t (c = *cis*, t = *trans*) refer to the positions relative to the first deuterium atom and also represent the values of the corresponding isotopic shifts. Using the recorded spectra[27] the estimated values of these shifts were found to be α = -17.9, β_c = -7.0, β_t = -8.3, γ_c = -1.9, and γ_t = -0.3 in units of parts per billion (p.p.b.). Mass spectrometric analyses of cyclopentane exchanged over three metals are shown in table 2.4. These proved to be typical of the metals used. Iridium, although giving products up to d_{10}, has as its main

product d_1-cyclopentane; rhodium exhibits two main products at d_1- and d_2-cyclopentane; and platinum has a maximum at d_5-cyclopentane. Comparison of these results with their respective deuterium nmr spectra, figure 2.4, demonstrates the compatibility of the two techniques.

Table 2.4

Cyclopentane Compositions for Comparison with ^2D nmr Spectra

	% Isotopic Species					
Metal	D_1	D_2	D_3	D_4	D_5	D_6 to D_{10}
Ir	62.6	22.9	6.0	3.6	2.4	2.4
Rh	34.1	29.4	14.3	9.5	6.4	6.4
Pt	32.9	17.1	8.6	8.6	24.3	8.6

As these results were of molecules which had only reacted once at the catalyst surface the main process by which two or more deuterium atoms were incorporated into the molecule would have been by the $\alpha\beta$-process, i.e. the interconversion of adsorbed cycloalkyl and cycloalkene intermediates with the subsequent substitution of the hydrogen atoms by deuterium on one side of the cyclopentane ring. Thus a d_2-cyclopentane species would probably be *cis*-1,2-dideuterocyclopentane, and the d_5-cyclopentane would probably correspond to complete replacement of the hydrogen atoms on one side of the ring.

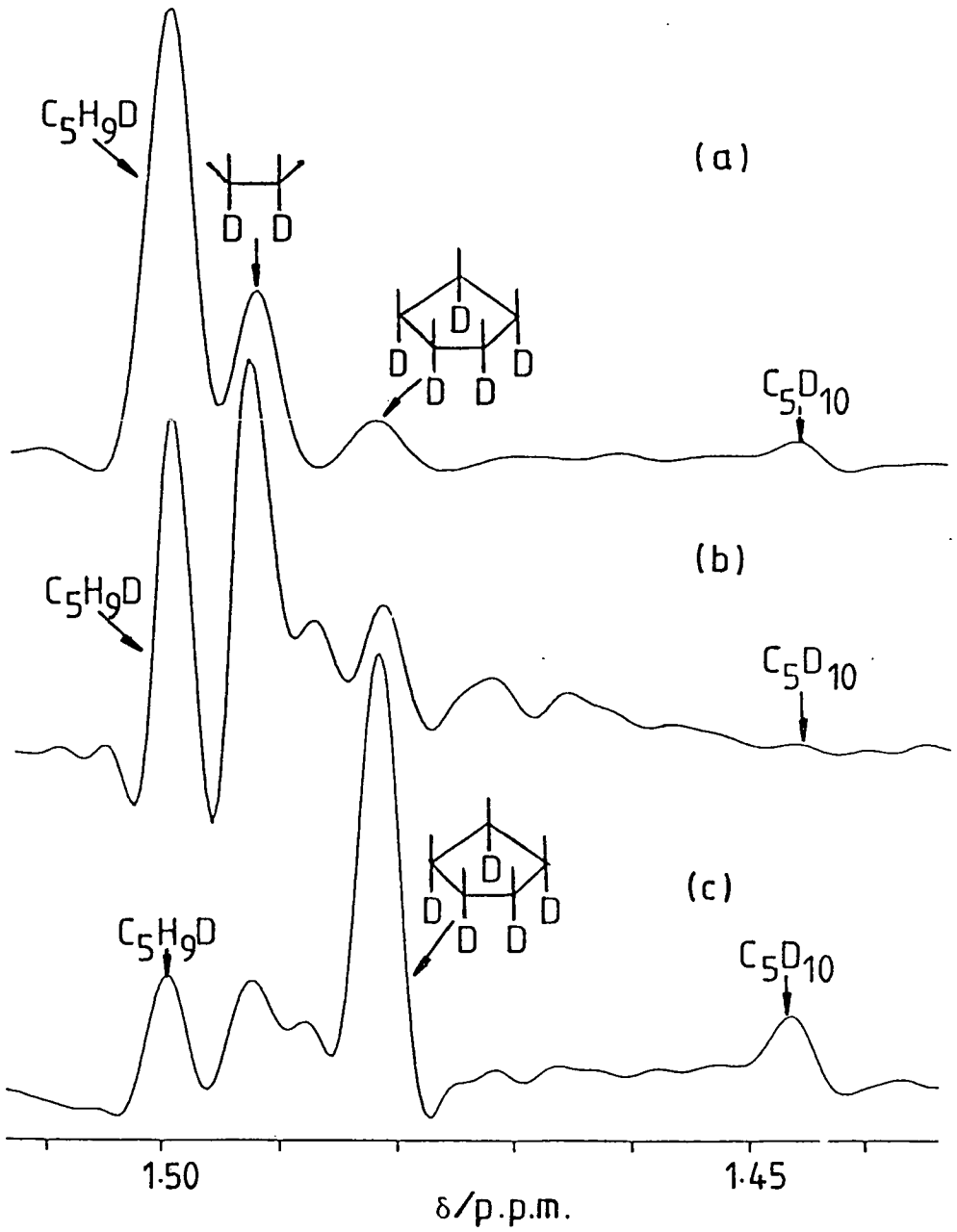


Figure 2.4 Deuterium nmr spectra of cyclopentane exchanged over (a) Ir, (b) Rh, and (c) Pt supported metal catalysts.

This latter assignment can clearly be seen for the exchanged cyclopentane products over the platinum catalyst which had a maximum at d_5 in the mass spectrometric data and a maximum in the ^2D nmr spectrum, figure 2.4(c), separated by -17.9 p.p.b. from the monodeuteroproduct (corresponding to $2\beta_C$ and $2\gamma_C$ interactions). This value unfortunately is very similar to that expected for an α-interaction where the deuterium atoms are bound to the same carbon atom, which would be the case if an $\alpha\alpha$-diadsorbed intermediate had participated in the exchange mechanism over rhodium to give the large amount of d_2-cyclopentane. Here it was not possible to give a quantitative assessment of the contribution of 1,1-d_2-cyclopentane in the presence of d_5-cyclopentane. However by using Monte Carlo methods and the calculated isotopic shifts it was possible to generate spectra by computer that reproduced the directly transformed deuterium nmr spectra assuming that the experimental results conformed to an $\alpha\beta$-exchange model[28]. Such a procedure indicated qualitatively that the amount of d_2-product formed on rhodium is not due to an $\alpha\alpha$-diadsorption process.

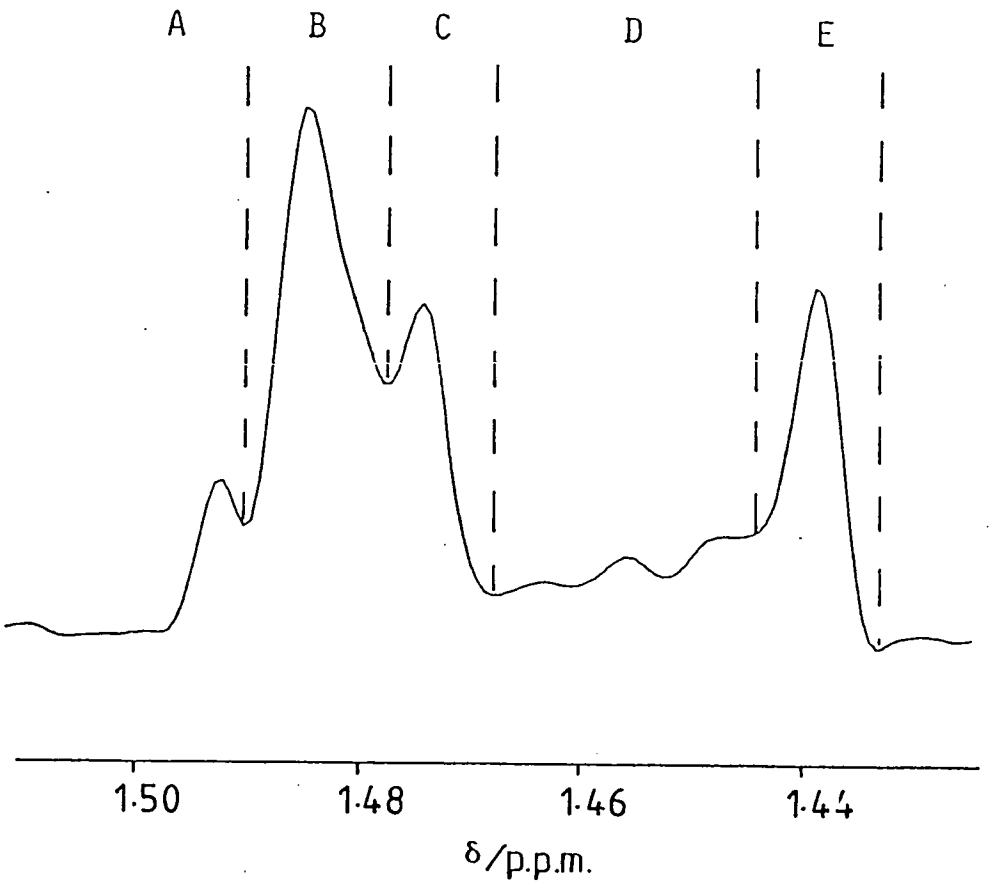


Figure 2.5 Line narrowed nmr spectrum for the cyclopentanes produced over Ni.

More recently a further study of the origin of the d_2-product from cyclopentane exchanged over silica-supported rhodium and nickel catalysts has provided evidence for the $\alpha\beta$-process on these catalysts in a more quantitative manner[29]. Both catalysts exhibited large amounts of d_2-cyclopentane as an initial product as indicated in table 2.5. Employing the previous results

Table 2.5

Products from Cyclopentane Exchange over Supported Rhodium and Nickel Catalysts

		% Alkane										
Metal	Temp./K	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}
Rh	273	93.1	3.0	2.5	0.7	0.4	0.2	0.1	0.0	0.0	0.0	0.0
Ni	332	91.8	1.5	2.6	1.2	0.7	0.8	0.2	0.2	0.2	0.3	0.5

Table 2.6

Correlation of NMR and Mass Spectrometric Results for Nickel

Peak or Section	Range of $-\Delta\delta$/p.p.b.	% D	Contributions assuming that D_2 is 1,2	Calculated %D: D_2 is 1,2-	Calculated %D: D_2 is 1,1-
A	-5.0 to 2.0	6	D_1	5	5
B	2.0 to 15.0	42	$2D_2$, $3D_3$, $4D_4$	40	22
C	15.0 to 22.0	18	$5D_5$, $2D_6$, D_7	16	34
D	22.0 to 470	15	$4D_6$, $6D_7$, $6D_8$, $5D_9$	16	16
E	47.0 to 58.0	19	$2D_8$, $4D_9$, $10D_{10}$	23	23

obtained from cyclopentane exchange[27] allowed assignment of the peaks in the line narrowed nmr spectrum from the nickel data to the contributing compounds, figure 2.5. In order to determine whether the d_2-product from nickel was 1,2- or 1,1-d_2-cyclopentane the percentages of deuterium found in the various nmr peaks were compared with the calculated distributions derived from the mass spectrometric data. As table 2.6 shows the comparison clearly favoured the assignment of 1,2- to the d_2-cyclopentane; a consequence of the reversible formation of $\alpha\beta$-diadsorbed species and not through $\alpha\alpha$-diadsorbed intermediates.

2.4 IDENTIFICATION OF HYDROCARBON INTERMEDIATES FORMED ON OXIDES : FURTHER STUDIES USING ^{2}D NMR

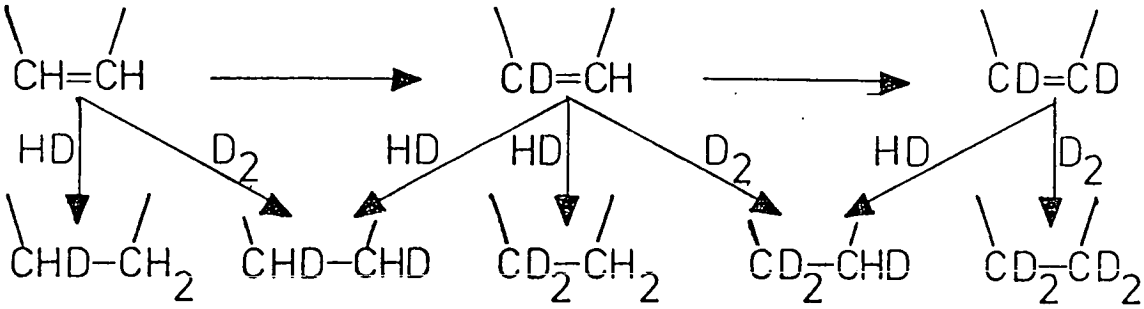
Dehydration of metal oxides at temperatures greater than 673K may activate hydrogen and hence promote hydrogenation reactions. The study of alkene exchange reactions with deuterium over such metal oxides has proved very useful in identifying the surface intermediates formed by the reacting alkene. Due to their inherent nature alkenes have been particularly amenable for study by microwave and nmr spectroscopy, thus the intermediates formed by simple alkenes on some oxides have been well established. In their study of cyclopentene exchange on alumina, Hightower and Hall[30] used proton nmr to show that deuterium was incorporated only into the alkene positions.

In a systematic study of propene exchange over a range of metal oxides microwave spectroscopy showed that depending on the oxide several intermediates could be formed which led to different exchanged products[31]. The use of ^{2}D nmr has also proved useful in studying the exchange reactions of cyclopentene[32] and 2-methylpropene[33]. Such studies cannot be easily analysed by other spectroscopic techniques.

2.4.1 Cyclopentene

At 355K cyclopentene exchange with deuterium occurred readily over zinc oxide[26]. The deuterium nmr spectrum of the exchanged cyclopentene exhibited only two resonances at values of δ = 5.78 and 2.31 p.p.m. (p.p.m. = parts per million) in ratios of about 50:1. This indicated that the majority of the deuterium atoms in the exchanged cyclopentene were in the alkenic position (δ = 5.78 p.p.m.) with a very small proportion in the methylene groups adjacent to the double bond (δ = 2.31 p.p.m.) and none in the remote methylene group (δ = 1.80 p.p.m.). A vinylic intermediate was proposed as responsible for exchange into the alkenic position and an allyl species for the small detectable amount of double-bond movement. This oxide catalyst also promoted the addition reaction, and, as previously mentioned, the resultant cyclopentane spectrum was readily reconciled with the acquired mass spectral data to establish that the reactions which

occurred on zinc oxide are as those shown in scheme 2.7.



Scheme 2.7 Reactions of cyclopentene on zinc oxide

Calcium oxide proved to be a highly efficient catalyst for cyclopentene exchange with all three positions alkenic, allylic and remote acquiring deuterium with equal probability[32]. This indicated that interconversion between an adsorbed alkene and a π-allyl species was an important mechanism accompanied by rapid double-bond movement. Comparison of deuterium nmr spectra of cyclopentene labelled with deuterium in the alkenic positions before and after self-exchange on calcium oxide confirmed that intermolecular scrambling of the cyclopentene hydrogens by interconversion of alkene to π-allyl species was indeed a very rapid process. This was the main cause for the ratios of the alkenic:allylic: remote positions in the cyclopentene being close to the equilibrium values of 1:2:1 in the normal exchange

experiments.

Further study of cyclopentene exchange over Al_2O_3[32] confirmed the earlier reports of Hightower and Hall[30] that the dominant process of exchange over this oxide was interconversion between alkene and vinyl intermediates with incorporation of deuterium only in the alkenic positions. The exchange reaction over MgO proved to be intermediate between these two extremes[32]. There was preferential exchange of the alkenic hydrogen atoms but there was also a significant contribution from interconversion to π-allyl species which gave appreciable exchange at the allylic positions and, to a more limited extent, in the remote positions. The probable intermediates involved in reactions of cyclopentene over oxide catalysts can be summarised, figure 2.6.

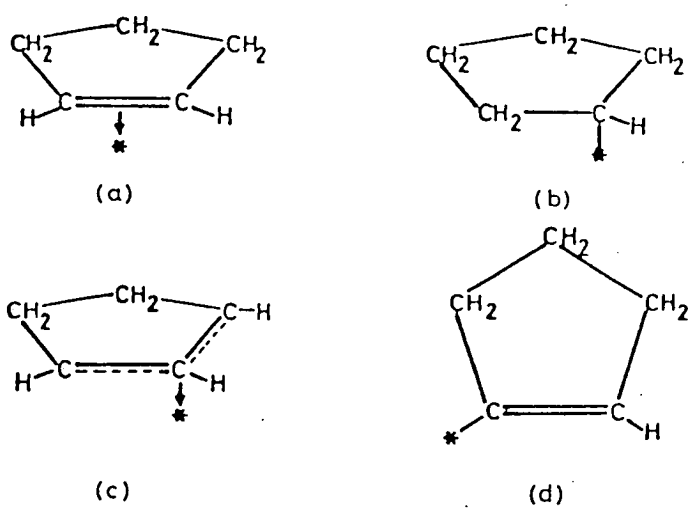


Figure 2.6 Probable intermediates formed on oxides from cyclopentene : 'horizontal species'; (a) alkene, (b) alkyl, (c) allyl; 'vertical' species (d) vinyl.

2.4.2 Propene

Propene exchange was also studied over calcium oxide[32]. The resultant ^2D nmr spectra, figure 2.7, indicated that only the hydrogens in the terminal positions were exchanged and that the incorporated deuterium was randomly distributed. This type of exchange

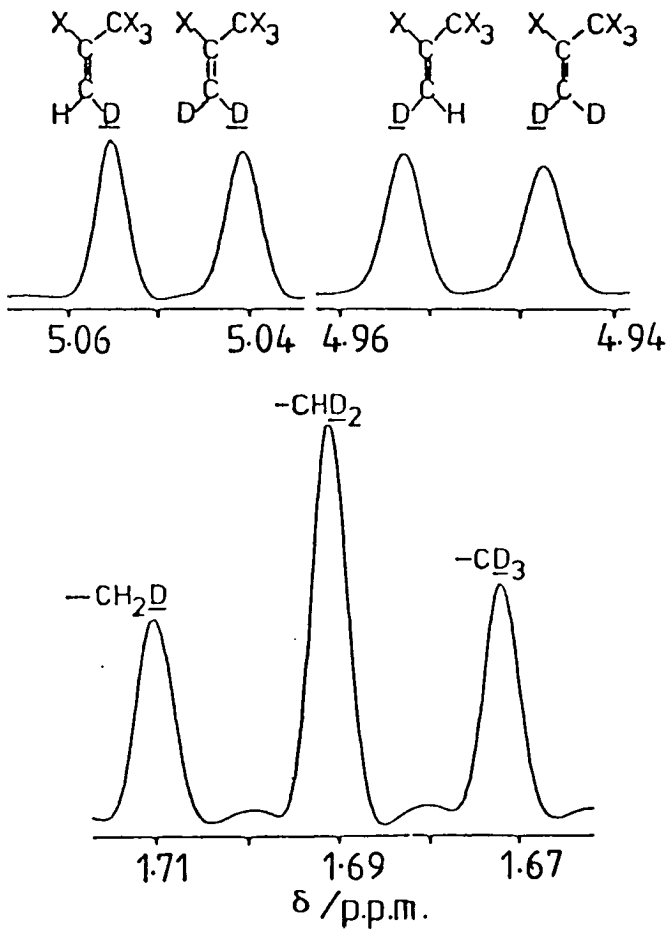


Figure 2.7 Deuterium nmr spectrum of propene exchanged over calcium oxide

can be attributed to the reversible formation of a symmetrically adsorbed intermediate (probably a π-allyl species). Similar results were found for La_2O_3 at 380K but in this instance there was also a small amount of exchange of the H atom on the central carbon atom[34]. Previously the products from the exchange of propene over Al_2O_3 had been examined using microwave spectroscopy[31]. Using ^2D nmr it was confirmed that the exchange involved propenyl and σ-allyl intermediates which resulted in the two ends of the molecule being exchanged to different extents. At 293K it was reported that 69% of the propene exchanged through a propen-1-yl intermediate and 31% through a σ-allyl species[32].

2.4.3 2-Methylpropene

The reaction products from exchange of this molecule with deuterium over metal oxides have also proved suitable for analysis by ^2D nmr. 2-Methylpropene exchange over basic oxides usually occurs in a stepwise fashion with all eight hydrogen atoms being equally exchangeable. The mechanism is thought to involve the reversible dissociation of the alkene to an adsorbed allyl species, a process that allows interconversion of methyl and methylene hydrogen and deuterium atoms as well as providing a route to the exchange of all eight atoms in the molecule. Deuterium nmr was used to study the

products of the alkene exchange reaction over CaO, γ-Al_2O_3, La_2O_3 and ZrO_2[33]. As the latter two oxides also showed some activity for the addition reaction, the resultant 2-methylpropanes were also analysed. The data showed that the deuterium in the exchanged 2-methylpropenes was randomly distributed throughout the molecule. There was a slight suggestion however that over alumina some preferential exchange of the methylene group occurred. Although there was little incorporation of deuterium into the alkene over ZrO_2 a value of 3:1 was found for the ratio of (deuterium in the methyl groups): (deuterium in the methylene group).

Analysis of the amounts and groupings of the deuterium in the products from the addition reaction over ZrO_2 indicated that the reaction approximated to the straightforward addition of D_2 to the alkene. In a similar analysis of the 2-methylpropane species formed over La_2O_3 the nmr results showed that the chances of the alkene acquiring deuterium at the primary and tertiary positions in the formation of the alkane differ. This was attributed to a surface depletion of deuterium due to the efficiency of the alkene exchange reaction.

2.5 CONCLUSIONS

The main discussion and conclusions concerning the exchange of deuterium with hydrocarbons over metal and oxide catalysts were reasonably well established prior to

the advent of high field deuterium nmr spectroscopy. However, by providing a means of identifying the groupings of deuterium atoms in the products of exchange reactions and of estimating quantitatively the distribution of the atoms in the various groupings, the results obtained by this technique have proved to be more revealing and have necessitated a revision of some of the accepted ideas about exchange mechanisms. This was particularly true for the cycloalkane exchange over rhodium and nickel catalysts where at low temperatures the large d_2-cyclopentane product was unequivocally shown to be *cis*-1,2- and not 1,1-dideuterocyclopentane. It is the intention of the present study to investigate the exchange reactions of other alkanes on a variety of supported-metals to determine whether ^2D nmr could further enhance our knowledge of the intermediates formed.

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CHAPTER 3

EXPERIMENTAL

3.1 INTRODUCTION

The main techniques used in this study were gas chromatography, mass spectrometry, and deuterium nmr spectroscopy. The present chapter describes the use of gas chromatographic and mass spectrometric techniques and the experimental procedures required for studying hydrocarbon reactions. The details of the analysis of the ^{2}D nmr spectra for the different hydrocarbons will be dealt with in the respective chapters. Other techniques used in individual parts of the present work of catalyst characterisation, i.e. temperature programmed reduction/desorption and pulse chemisorption, are dealt with in the relevant chapter, as are catalyst preparation methods.

3.2 APPARATUS

3.2.1 Gas Handling Lines

Three separate vacuum lines were used in these studies, the essential differences being in the type of reactor and/or the analytical method used to monitor the course of reaction. Two of the lines were equipped with a static reactor and the third with a closed recirculating system. All three reactors were attached to conventional gas-handling lines[1,2]. A line diagram of line 2 with a

static glass reactor which was connected to a gas chromatograph is shown in figure 3.1. This line was used for analysis of the products from hydrogenolysis reactions. Line 1, which was connected to a mass spectrometer, was fitted with greaseless taps (Springhams Ltd.) whereas lines 2 and 3 used conventional ground glass stopcocks lubricated with Apiezon L vacuum grease.

The vacuum systems were constructed of Pyrex glass and evacuated via an electrically heated three-stage mercury diffusion pump backed by an Edwards ED50 oil rotary pump. Each line consisted of two of these series of pumps, one for the gas handling section and the other for the reaction section. Each section could then be evacuated separately. Mercury contamination was prevented by having cold traps cooled in liquid nitrogen between the diffusion pumps and the vacuum lines. These pumping systems allowed pressures of *ca.* 10^{-3} Pa to be attained. The pressure was frequently checked before and after pretreatment of the catalysts, using a McLeod gauge, to ensure that the best possible vacuum was maintained.

Diaphragm pressure gauges (Leybold-Heraeus) were employed when making up reaction mixtures. These were marked in Torr (*1* Torr = 133.2 Pa) and were further calibrated against a mercury manometer. The constituents of the reaction mixtures, which were prepared in the mixing volume, were either stored in the permanently mounted glass bulbs or fed into the system via ground

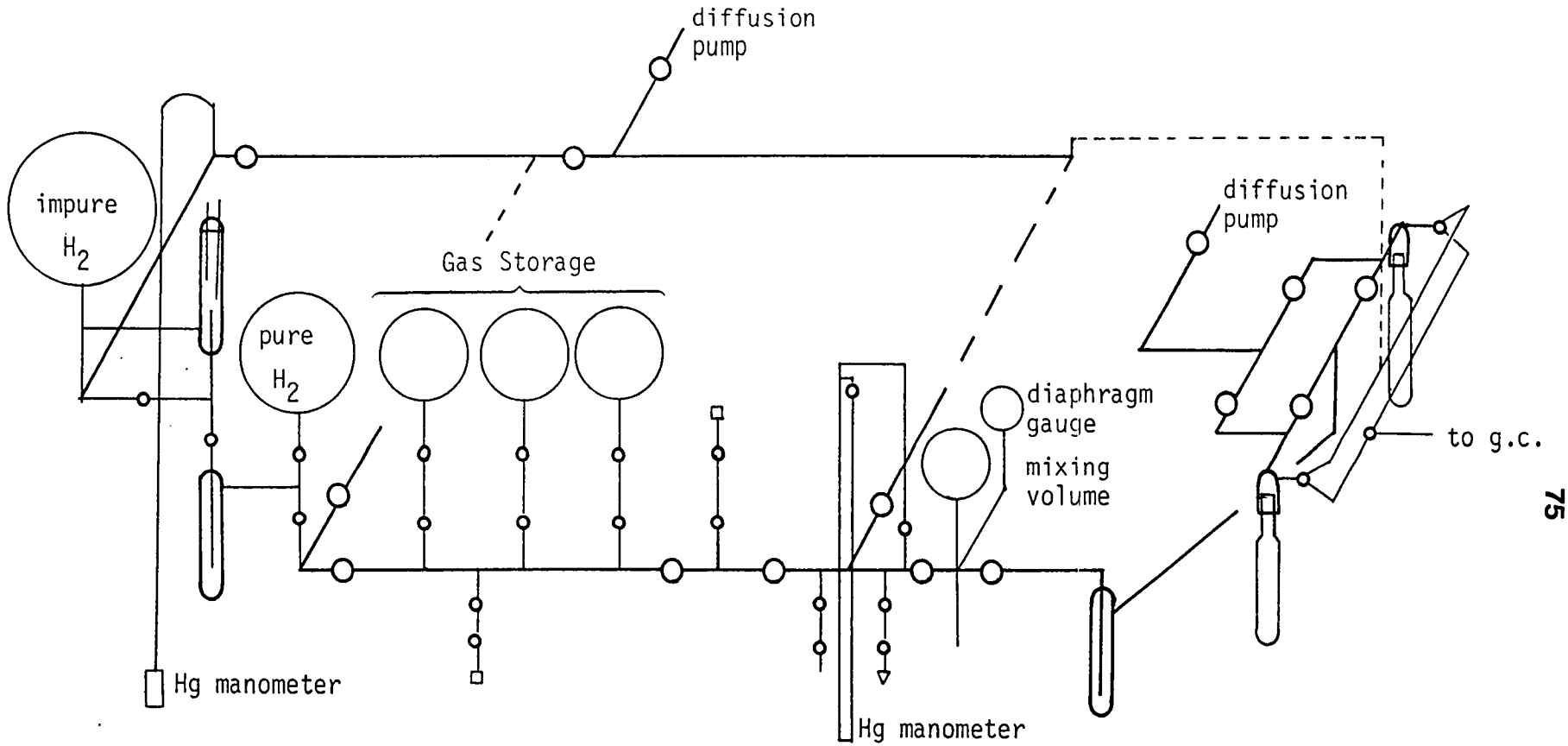

Figure 3.1 Line diagram showing conventional gass handling line fitted with a static reactor.

glass joints from small glass reservoirs fitted with teflon Rotaflo taps.

The volumes in the vacuum lines such as the mixing volume and the reactor volume were calibrated by successive expansions of air from a bulb of known volume and applying Boyle's law ($P_1V_1 = P_2V_2$). This information was necessary to calculate the pressure of hydrocarbon over the catalyst after expansion of the reactants from the mixing volume into the reactor volume.

On each of the vacuum lines purification of hydrogen or deuterium was achieved by passage through a heated Pd-Ag alloy thimble and then over a cold trap at liquid nitrogen temperature. The purified gas was then kept in a permanent glass storage bulb until required.

3.2.2 Reaction and Sampling Systems

The static reaction vessels used on lines 1 and 2 were of similar design and size, a diameter of 0.04 m and an approximate length of 0.12-0.15 m. The vessel used on the greaseless vacuum line, line 1, was attached by means of a Young's B24 greaseless joint, the socket being encased in a water-cooled jacket and the connection being made airtight by a neoprene 'O' ring fitted on the grooved cone. Ground glass joints of the same size were used for the static reactors which fitted on line 2. Depending on the temperature of the catalyst the vessels were constructed of either silica or pyrex glass, the former

being used when temperatures of >723K were required. In order that the catalysts could be reduced prior to an experiment they were pretreated in flowing hydrogen which exited via a glass tube containing a teflon Rotaflo tap. The reaction vessel also contained a thermocouple well to allow monitoring of the temperature. Figure 3.2 illustrates the essential features in the static reaction vessel.

A diagram of the recirculation system is shown in figure 3.3. The recirculation of the reactant mixture was achieved with an all metal reciprocating pump manufactured by the Metal-Bellows Corporation (MB21E). A maximum flow rate of $0.8 l(min)^{-1}$, measured by a floating head rotameter incorporated into the recirculation system, was always used to ensure that reaction rates were not limited by the pumping speed. The reaction vessel, which held the catalyst sample on a 10 mm sintered disk, was connected to the system by ground glass spherical joints using lock-style clips as well as Apiezon T vacuum grease. A small thermocouple well allowed the temperature of the catalyst to be followed. The reaction system was connected to both a mass spectrometer and gas chromatograph.

The reaction vessels were heated by a close-fitting electrical furnace: essentially a silica tube approximately 0.06 m in diameter wound with resistance wire. The wiring was insulated using a non-conductive,

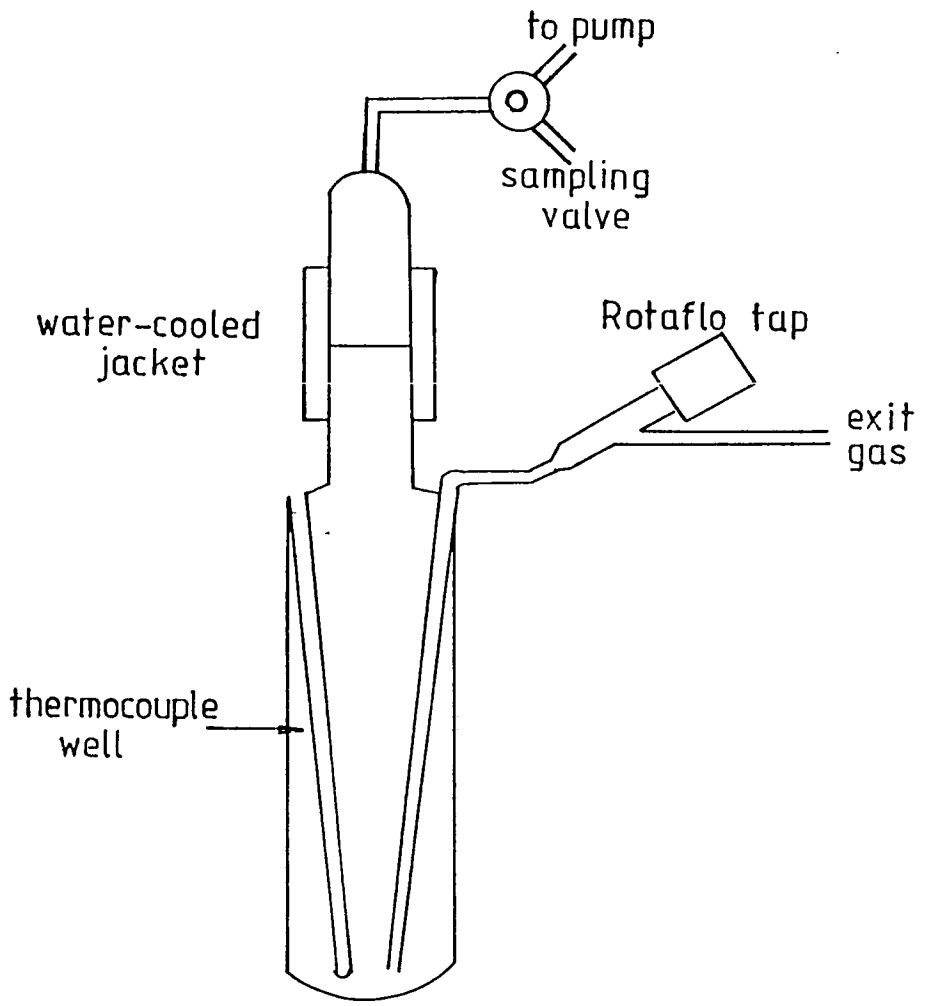

Figure 3.2 A static reaction vessel.

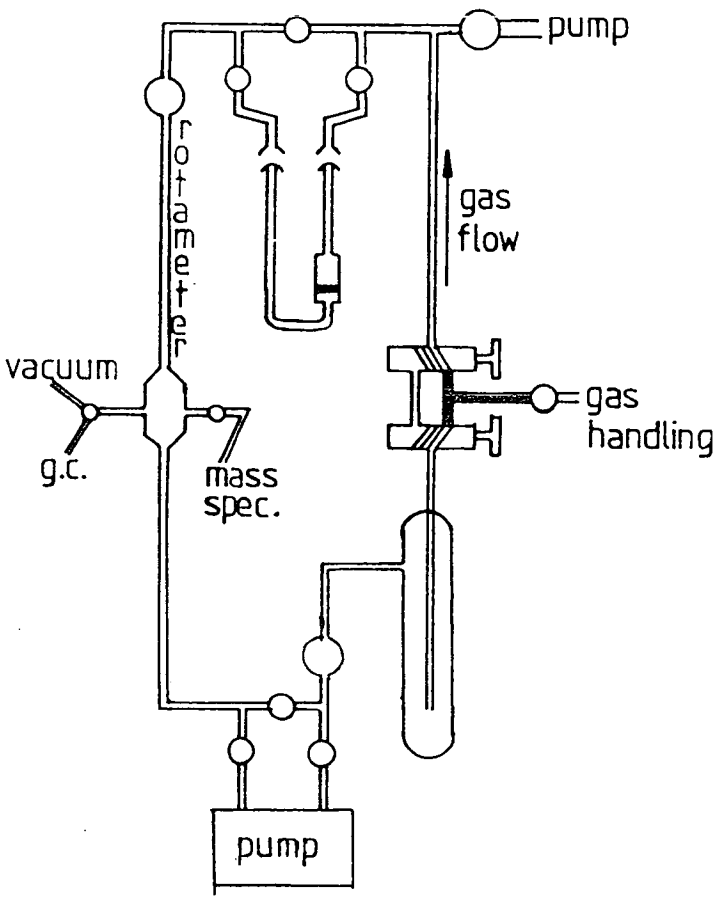

Figure 3.3 Recirculation system which was connected to both a mass spectrometer and gas chromatograph.

heat-resistant cement and was further enclosed in a metal container packed with heating insulation. The temperature of the furnace was controlled by a Eurotherm proportional controller fitted with a chromel-alumel thermocouple, this could maintain a steady temperature within 1K. The actual temperature of the catalyst was recorded from a chromel-alumel thermocouple inserted into the thermocouple wells of the reaction vessels. The thermocouple was connected to a Comark 5000 digital thermometer.

The reaction vessels of lines 1 and 3 were connected to a mass spectrometer via a capillary leak which allowed a loss of about 2-3% $(hour)^{-1}$ of the reaction mixture. The reaction vessels of lines 2 and 3 were connected to gas chromatographs via a three-way tap and a six-way gas sampling value (Carle Instruments, Inc.). Figure 3.4 shows a schematic of the operation of the sampling system employed on line 3. The small internal volume of the sampling valves and sample loop, and the use of capillary tubing allowed the sample loss of gas from the reacting material to be restricted to approximately 1% $(sample)^{-1}$.

3.2.3 Gas Chromatography

Analyses of the reaction mixtures in lines 2 and 3 were performed with Perkin-Elmer F.33 gas chromatographs fitted with a flame ionisation detector. The samples from the reaction mixtures were flushed from the sample loop by the carrier gas onto a packed column where the different

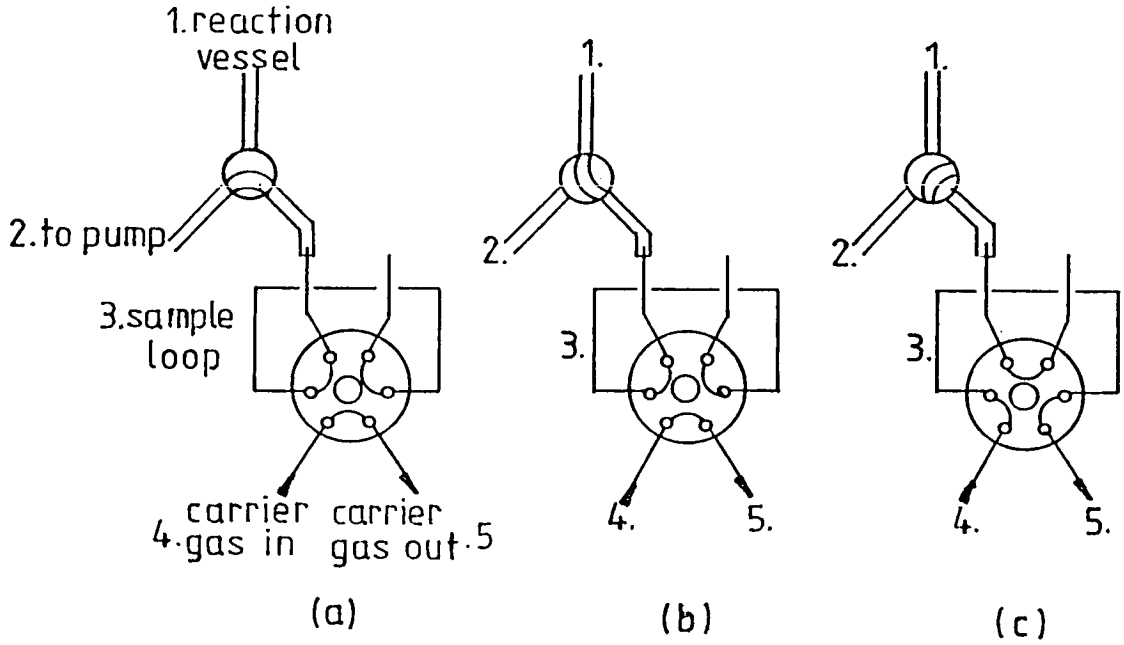

Figure 3.4 Operation of sampling system.

(a) evacuation of sample loop

(b) expansion of reactants into sample loop

(c) sampling to gas chromatograph.

partition ratios between the stationary and mobile phases caused the components of the reaction mixture to travel at different rates. When the gases reach the flame ionisation detector, which consists of a hydrogen flame, they are ionised and the conductivity of the flame is changed. A voltage applied across this flame produces a current which is amplified and recorded.

The stainless steel column used for the C_5 hydrogenolysis experiments carried out on line 2 was 4m x 0.32mm o.d. and contained 15% OV101 w/w on Chromosorb W. It was operated at room temperature with a nitrogen carrier gas pressure of 8 p.s.i.g. and under such conditions all the hydrocarbons present were separated in twelve minutes. The chromatogram was displayed on a Servoscribe potentiometric recorder and a digital print-out of the peak areas and retention times was provided by a Hewlett-Packard Integrator (Model No. 3373b). The alkene and alkane reaction mixture in the 2-methylpropene addition reactions was separated on a 2 m x 0.32mm o.d. stainless steel column containing 3% w/w squalane on activated alumina. This was operated at 393K with a nitrogen carrier gas pressure of 35 p.s.i.g. which allowed the two peaks to be adequately separated in 10 minutes. A Perkin-Elmer computing integrator (LCI-100) was used to record and calculate the percentage hydrocarbon compositions.

3.2.4 Mass Spectrometry

In the exchange reactions continuous sampling from the reaction vessel was accomplished via a capillary leak connected to a Vacuum Generators Micromass 601 mass spectrometer (a fast scanning 90° magnetic sector instrument). Gas molecules entering the analyser were ionised by subjecting them to bombardment by a controlled beam of electrons from a tungsten filament. Different ionising voltages were used for different hydrocarbons with a compromise being achieved between adequate sensitivity and minimum mass spectral fragmentation. Although the spectra were latterly corrected for peaks arising from loss of hydrogen or deuterium from the parent ions the errors in evaluating the spectra were minimised by keeping fragmentation to a minimum. The conditions selected for the various hydrocarbons investigated will be reported in the relevant chapters.

The mass region around the parent ion of each hydrocarbon and their respective deuterated derivatives was scanned by varying the magnetic field strength while keeping the ion accelerating voltage constant. The ions were detected by means of a Faraday cup or electron multiplier and the spectra recorded on a fast response potentiometric recorder (Kipp and Zonen, BD40). Typically in this work a range of interest might be fifteen mass units which could be scanned in approximately four minutes. The heights of the peaks were measured manually

to the nearest 0.5 mm and the dynamic range attained (ratio of the largest intensity to the smallest intensity measured) was of the order of 10^4.

3.3. EXPERIMENTAL PROCEDURE

The reaction vessel containing the desired amount of catalyst was attached to the line and evacuated to a pressure of 10^{-3} Pa. Cylinder hydrogen (B.O.C.) was then admitted to the gas handling system and reaction vessel with the increase in pressure being monitored by a mercury manometer. When the pressure reached one atmosphere the teflon tap connected to the outflow tube on the reaction vessel was opened allowing the hydrogen to continuously flow over the catalyst. The hydrogen was purified by passage through a 'deoxo' unit (Englehard Industries Ltd.) and two molecular sieves, one at ambient temperature and the other at liquid nitrogen temperature. The temperature and length of catalyst reduction varied according to the appropriate experiment, details are given in the relevant chapters. After reduction the hydrogen flow was stopped and the gas handling and reaction vessels evacuated. The catalyst was then typically evacuated at, or 50° above, the reduction temperature for a 30 minute period and then cooled to the required reaction temperature under a dynamic vacuum.

The preparation of reaction mixtures adopted the following procedure: the required amount of hydrocarbon

was expanded into the mixing volume where it was degassed by a freeze-thaw cycle and then condensed. Hydrogen or deuterium, usually in 5- or 10-fold excess, was then expanded into the mixing volume. This was isolated and the gases allowed to stand for >30 minutes at ambient temperature to ensure a homogeneous gas mixture. The reactants were expanded into the reaction vessel which was isolated. The reaction was then monitored for up to 2.5 hrs or until the required amount of reaction had occurred.

For experiments carried out specifically to prepare samples for subsequent analysis by ^{2}D nmr on line 1, the reactants were expanded back through a cold trap at liquid nitrogen temperature into an evacuated large storage bulb and allowed to stand for a period of time, sometimes overnight. The deuterium was slowly evacuated and the remaining hydrocarbon degassed before distilling it into a 5 mm nmr tube containing 0.5 cm^3 5% D-chloroform and the tube sealed. On the recirculation system the reactants were isolated from the catalyst and the hydrocarbon condensed in the cold trap, see figure 3.3.

3.4 TREATMENT OF DATA

3.4.1 Hydrogenolysis Reactions

As the peak areas obtained from flame ionisation detectors are approximately proportional to the weight of hydrocarbon injected into the gas chromatograph, sensitivity factors for each hydrocarbon were determined

from calibration graphs of chromatographic peak area against hydrocarbon pressure in the sampling loop. If the sensitivity of the C_5 hydrocarbon is arbitrarily defined as unity the other hydrocarbons have the sensitivity factors shown in table 3.1. The amounts of hydrocarbon products were expressed as a percentage of the total carbon content of the gases present.

e.g. for methane

$$\%C_1 = \left[\frac{\frac{C_1}{C_5} \cdot A_1 f_1}{\sum_{i=1}^{i=5} \frac{C_i}{C_5} \cdot A_i f_i} \right] \times 100 \qquad \text{equ. 3.1}$$

where A_i and f_i are the peak areas and sensitivity factors of the hydrocarbon with C_i carbon atoms.

Table 3.1

Relative Sensitivities of Hydrocarbons

Hydrocarbon	M_w[a]	R_t[b] (mins)	Sensitivity
methane	16	2.10	4.815
ethane	30	2.38	2.503
propane	44	3.08	1.718
2-methylpropane	58	4.22	1.289
butane	58	5.23	1.284
2-methylbutane	70	9.30	1.000
n-pentane	70	12.63	1.000

[a] Molecular weight

[b] Retention time of hydrocarbon in gas chromatograph

Plots were made of the moles of each product formed against the number of moles of reactant consumed. The slopes of such lines at low conversions were used to determine the selectivities, S_i, for the products. The method employed to evaluate the quantity, M_b, where M_b represents the depth of hydrogenolysis, is best illustrated with reference to the reaction of 2-methylbutane.

$$M_b = \sum_{i=1}^{i=4} S_i \quad / \ (1 - S_s) - 1 \qquad \text{equ. 3.2}$$

where S_i represents the moles of the product with i carbon atoms formed for each mole of reactant consumed. Equation 3.2 as defined makes allowance for reactant isomerised to n-pentane (S_s). Rates of reaction were determined from plots of reactant concentration against time and are expressed as molecule s^{-1} (metal atom)$^{-1}$.

3.4.2 Exchange Reactions

Experimental data consist of several sets of spectra taken at regular time intervals each containing a number of peaks of varying intensity corresponding to species of different masses. The measured peak heights were fed into a computer program[3] which corrected the spectra for the contribution of natural isotopes and for fragmentation

arising from loss of hydrogen or deuterium from the parent ions. The program takes into account that molecules containing deuterium have a smaller tendency for fragmentation and that there is a greater chance of loss of hydrogen as compared to deuterium from parent ions containing both types of atoms[4]. The reliability of the fragmentation corrections was assessed by comparing the fragment peak intensities in the corrected spectra with those in the raw spectra. After correction, fragment peak intensities should ideally be reduced to values close to zero but residual values corresponding to less than 10% of the fragment intensities in the raw spectra were considered acceptable. The program calculated a percentage d_n vs. n distribution (where d_n refers to an isotopic species containing n deuterium atoms).

The treatment of the product distributions has been detailed elsewhere[5] and is only briefly described below.

The course of an exchange reaction can be followed in two ways, either in terms of the rate of incorporation of deuterium into the molecule or in terms of the rate of disappearance of the light hydrocarbon. The latter rate constant, k_o, is defined by the equation

$$-\log(x_o - x_\infty) = \frac{k_o t}{2.303(100-x_\infty)} - \log(100-x_\infty) \qquad \text{equ. 3.3}$$

where x_o, is the percentage of light hydrocarbon present at time t, and 100 and x_∞ are the initial and final

percentages respectively. Thus a first-order plot of $\log(x_o - x_\infty)$ *vs.* time (t) will yield a straight line with gradient equal to $-k_o/2.303\ (100-x_\infty)$. In practice the equilibrium concentration of light hydrocarbon, x_∞, can be neglected in the calculation of initial rates.

The deuterium content of a hydrocarbon is defined by the parameter ϕ,

$$\phi = \sum_{i}^{n} i d_i \qquad \text{equ. 3.4}$$

where d_i is the percentage of hydrocarbon with n exchangeable hydrogens of which i are deuterium. The rate of entry of deuterium into the hydrocarbon is given by

$$-\log(\phi_\infty - \phi) = \frac{k_\phi t}{2.303\,\phi_\infty} - \log(\phi_\infty - \phi) \qquad \text{equ. 3.5}$$

where k_ϕ is a rate constant equivalent to the number of deuterium atoms entering 100 molecules of hydrocarbon in unit time and where ϕ_o and ϕ_∞ are the initial and equilibrium values of ϕ respectively. An estimate of ϕ_∞ based on the assumption that in the equilibrium distribution the hydrogen and deuterium are randomly distributed in the hydrocarbon and "hydrogen" mixture is given by

$$\phi_\infty = x_D.n.100 \qquad \text{equ. 3.6}$$

where x_D is the fraction of deuterium atoms in the total number of hydrogen and deuterium atoms in the system and n is the total number of exchangeable hydrogens in the hydrocarbon.

The ratio of the two rate constants

$$M = \frac{k_\phi}{k_o} \qquad \text{equ. 3.7}$$

where M is called the multiplicity of the reaction, is a useful parameter as 'it represents the mean number of hydrogen atoms replaced by deuterium atoms in each hydrocarbon molecule undergoing exchange in the initial stages of reaction. Values of M close to one indicate that only one hydrogen is exchanged per adsorption-desorption cycle, i.e. a stepwise exchange reaction. Multiple exchange is characterised by M values significantly greater than unity. Stepwise exchange may also be characterised by isotopic distributions which remain essentially binomial throughout the reaction.

The binomial distribution corresponds to the expansion of

$$100(h + d)^n \qquad \text{equ. 3.8}$$

where h and d are the probabilities of any hydrogen atom being H or a D atom respectively and n is the total number of exchangeable hydrogen atoms in the hydrocarbon. The probabilities h and d are defined by

$$d = \frac{\phi}{n.100} \qquad \text{equ. 3.9}$$

and $h = (1-d)$ equ. 3.10

3.5 SOURCE AND PURITY OF REAGENTS

The source and initial purity of each of the reactants used in these studies are listed in table 3.2. The hydrocarbons were further purified by retaining the middle fraction collected after several freeze/thaw cycles. The lighter hydrocarbons were stored on line and the liquid samples were kept in detachable reservoirs fitted with Rotaflo teflon taps and ground glass joints. The purification of hydrogen and deuterium was described previously.

Table 3.2

Source and Purity of Reactants

Reactant	Grade	%Purity	Supplier
Hydrogen			BOC Ltd.
Deuterium	C.P.	99.8	Matheson
Ethane	C.P.	99.3	
Propane	Instrument	99.5	
Propene	C.P.	99.5	
Butane	Instrument	99.5	
2-Methylpropane	C.P.	99.0	
2-Methylpropene	C.P.	99.0	
Pentane	Research	99.9	BDH
2-Methylbutane	Research	99.5	BDH
2,2-Dimethylpropane	C.P.	99.5	Matheson
2,2,3,3-Tetramethylbutane	-	99.0	Aldrich
2,2,4,4-Tetramethylpentane	API	-	**

** Sample kindly provided by Prof. J.K.A. Clarke

3.6 NMR SPECTROSCOPY

Deuterium nmr spectra appear, under broad-band proton decoupling, as stick spectra each anisochronous deuteron giving rise to one resonance peak and the corresponding shifts parallel the proton ones. As deuterium shifts are typically of the same order or less than the width of the resonances, a very high field nmr spectrometer combined with computer line narrowing is required to obtain sufficient resolution for measurement. The deuterium nmr spectra produced in this work were obtained using a Brüker WH360 spectrometer operating at 55.28 MHz using the Aspect 3000 data system. The presence of 5% D-chloroform in the solvent provided sufficient signal for optimisation of the homogeneity of the sample on the FID from a single 90° pulse and provided an internal reference taken as δ = 7.25 p.p.m. Spectra were obtained at 298K in the unlocked mode and broad band λ^{proton} decoupling (1.25 W) was employed unless otherwise stated. Satisfactory signal to noise was normally obtained from *ca.* 200 transients using a 70° pulse, spectral width of 500 Hz and 8K data points corresponding to an acquisition time of 8.2s. The data table was expanded to 64K data points before Fourier transformation of the accumulated decay signal, thus giving a digital resolution of 0.006 p.p.m. (0.016 Hz) per point.

In most cases it was not possible to determine the resonance positions accurately from the directly

transformed spectra since the small isotopic shifts observed were comparable with the natural widths of the resonance lines. So line-narrowed spectra were also obtained by multiplication of the accumulated decay signal by a double exponential function before expansion of the data table. This required careful selection of the function parameters (LB and GB in the Brüker nmr program FTQ 820601) in order to optimise resolution without the introduction of spurious maxima. As an example figure 3.5 shows the ^2D nmr spectra with and without line-narrowing for the cyclopentanes produced from exchange over Ir/Al_2O_3[6]. The ^2D nmr spectra shown in the present work unless otherwise stated have all been line-narrowed to improve resolution. The spectra were obtained through the S.E.R.C. high field facility at Edinburgh.

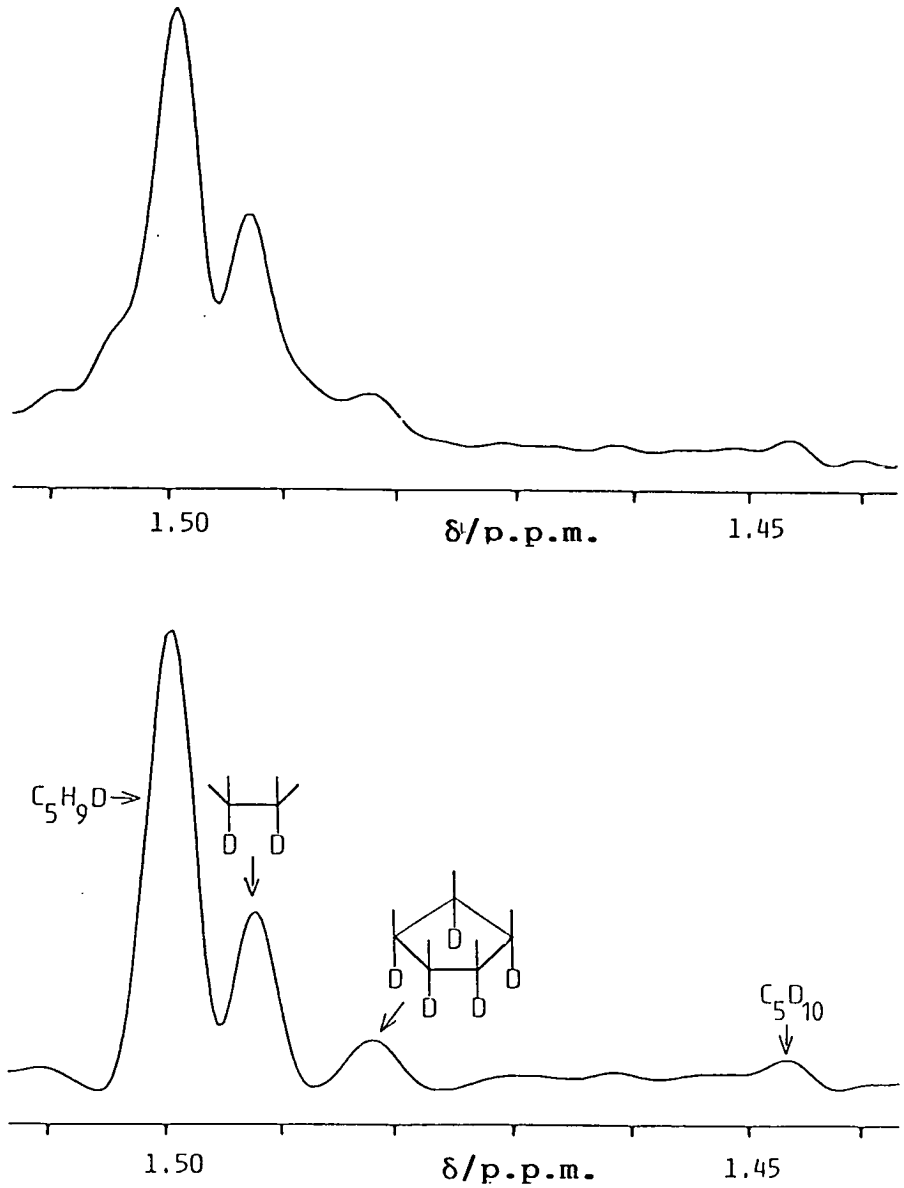

Figure 3.5 ^2D nmr spectra for cyclopentane exchange over Ir/Al_2O_3

(a) without line-narrowing

(b) with line-narrowing using LB=-0.5, GB=0.4.

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CHAPTER 4

HYDROCARBON REACTIONS OVER PLATINUM AND RHODIUM SUPPORTED ON NIOBIA

4.1 INTRODUCTION

As already discussed in section 1.7 the bulk of the research activity into strong metal-support interactions (SMSI) has concentrated on group VIII metals supported on titania and relatively few studies have examined the role of niobia as a support. In an attempt to redress this situation the present chapter describes work carried out with niobia as a support, for both platinum and rhodium. The catalysts were characterised using temperature programmed reduction (TPR) and temperature programmed desorption (TPD) and their catalytic activities in both 'non-SMSI' and 'SMSI' states were investigated using hydrogenolysis, a structure-sensitive reaction, of n-pentane and 2-methylbutane. A less structure-sensitive reaction, deuterium exchange of 2-methylbutane, was also studied over the Pt/Nb_2O_5 catalyst. In order to supplement the work on the niobia-supported catalysts results were also collected for a titania-supported platinum so that a direct comparison of the two supports could be made.

4.2 EXPERIMENTAL

4.2.1 Catalyst Preparation

A common approach used for the preparation of dispersed metal catalysts is impregnation[1,2]. This is achieved by filling the pores of the chosen support with a solution of the metal salt with subsequent evaporation of the solvent. The catalyst is prepared either by spraying the support with a solution of the metal compound or by adding the support material to a solution of a suitable metal salt such that the required weight of the active component is incorporated into the support without the use of excess solution of the salt. This is then followed by drying and subsequent decomposition either by thermal decomposition or reduction, at an elevated temperature.

The salts used in the preparation of the platinum and rhodium catalysts were H_2PtCl_6 and $RhCl_3$ respectively, supplied by Johnson-Matthey. One gram of each was added to a 10 cm^3 volumetric flask and dissolved in double-deionised water. The required amounts of solution to make 1% w/w supported catalysts were then extracted and added to more double de-ionised water so that the total volume was sufficient to give incipient wetness of the support. This had been judged earlier to be 0.6 $cm^3\ g^{-1}$ and 0.9 $cm^3\ g^{-1}$ for the titania and niobia supports respectively.

The titania used was pure anatase (0.4% rutile) and was supplied by Tioxide International Ltd. The niobia was

from Companhia Brasileira de Metalurgia e Minercão, and similar to material described by Iizuka *et al.*[3]. This was washed several times in distilled water before using. As the catalysts were to be subjected to a temperature of 773K, the supports, prior to impregnation, were calcined at this temperature overnight (16 hrs), to ensure that no subsequent agglomeration of the oxides occurred. Measurements of the oxide surface areas, by the B.E.T. method, gave values of 62 $m^2\ g^{-1}$ and 48 $m^2\ g^{-1}$ for the TiO_2 and Nb_2O_5 respectively.

The wetted supports were dried at room temperature for 24 hrs and then calcined overnight at 383K. This decomposition of the metal salt to yield the metal oxide which can then be reduced to the metal in hydrogen is an important step in the preparation of a catalyst. As the literature on Group VIII metals on transition metal oxides indicates, the step can be undertaken in several different ways. Simply reducing the salt on the oxide at the predetermined temperatures of 523K, a low temperature reduction (LTR) and 773K, a high temperature reduction (HTR), using flowing hydrogen just prior to any experiment was the procedure adopted by several authors[4]. Other reporters favoured the calcination of the supported metal precursor - in either pure oxygen or an oxygen/inert gas mixture. This latter process was favoured by Vis *et al.*[5] who termed the process "passivation". By oxidising the metal particles using an O_2/N_2 gas mixture after flushing

with N_2, the authors considered that they had prevented the uncontrollable effects of the first contact between air and the reduced metal catalyst. A high temperature reduction of their catalysts was carried out on the prepared Rh/TiO_2 catalysts before the passivation treatment and storage. Subsequent chemisorption experiments showed normal behaviour for a low temperature reduction implying that passivation and storage in air had nullified any metal-support interaction the initial HTR may have induced.

Another treatment of prepared catalysts quite similar to the above is outlined by Resasco and Haller[6]. They reduced their catalyst at 773K and oxidised it at 673K and claimed that the treatment gave a reproducible particle size.

The procedure adopted in the present study was to reduce the catalyst in bulk at 773K in flowing hydrogen (50 cm^3 min^{-1}) for 2 hours, evacuate and cool to room temperature. Pure oxygen was then allowed to flow over the catalyst which was heated to 673K and kept at this temperature for a further 2 hours. After cooling to room temperature in oxygen the catalyst was sieved to <150 μm, transferred to a sample bottle and stored in a desiccator until required.

4.2.2 Characterisation

Reduction of the metal oxide to the active component

is an important activation step in the preparation of supported metal catalysts. The recently developed technique of temperature-programmed reduction (TPR) can be used to characterise this process[7,8]. During TPR, a hydrogen containing gas is continuously flowed over the sample while the temperature is raised linearly with time. By measuring the consumption of hydrogen as a function of temperature a reduction profile is obtained. Such profiles provide 'fingerprints' of the chemical nature and environment of the catalytic component. Furthermore, the area under the TPR peak is a measure of the concentration of that component present on the catalyst surface.

The amount of exposed metal on the support, i.e. the dispersion, was estimated from temperature-programmed desorption (TPD) and pulse chemisorption experiments. In TPD the catalyst, following reduction, is exposed to hydrogen which is then desorbed into an inert gas stream as the temperature of the catalyst is raised linearly. From measurement of the amount of hydrogen desorbed the amount of exposed metal can be calculated. The catalyst can be exposed to hydrogen in two ways: (1) by flowing hydrogen over the catalyst; or (2) by pulse injections of hydrogen into the inert gas stream. In favourable circumstances the amount of hydrogen taken up by the catalyst from these pulses can also be estimated giving an alternative measure of dispersion. Although both methods were adopted in the present work, the data from the

adsorption of hydrogen by the pulse method was favoured.

A line diagram of the apparatus used for these techniques is shown in figure 4.1. In TPR, the reducing gas was 5% H_2 in argon and the profiles were monitored up to a maximum of 773K from 233K for the supported platinum catalysts and from 293K in the case of rhodium. For the TPD experiments hydrogen was allowed to flow over the catalyst for 30 minutes to ensure saturation before switching over to the argon carrier gas. Oxygen impurities were reduced to <1 p.p.m. by use of a molecular sieve and an "Oxy-trap" (Alltech Ltd.). Pulses of hydrogen were injected from a six-port gas sampling valve (Perkin Elmer Ltd.), with an internal volume of 0.16 cm^3, upstream from the catalyst.

The signals from the thermal conductivity detector (Perkin-Elmer Ltd. F.33 gas chromatograph) were recorded on a Kipp and Zonen (BD9) potentiometric twin-pen recorder and a microcomputer which was used to manually integrate the peak areas. A small furnace (Stanton Redcroft, model No. LMVS 100), controlled by a Stanton Redcroft UTP temperature-programmer, was used to heat the sample at 10K min^{-1} and 20K min^{-1}, during the TPR and TPD experiments respectively. The actual temperature of the sample was separately monitored by a chromel-alumel thermocouple connected in parallel to a digital thermometer (Comark 3000) and the potentiometric recorder. The thermocouple was placed in a small well in the reactor beside the

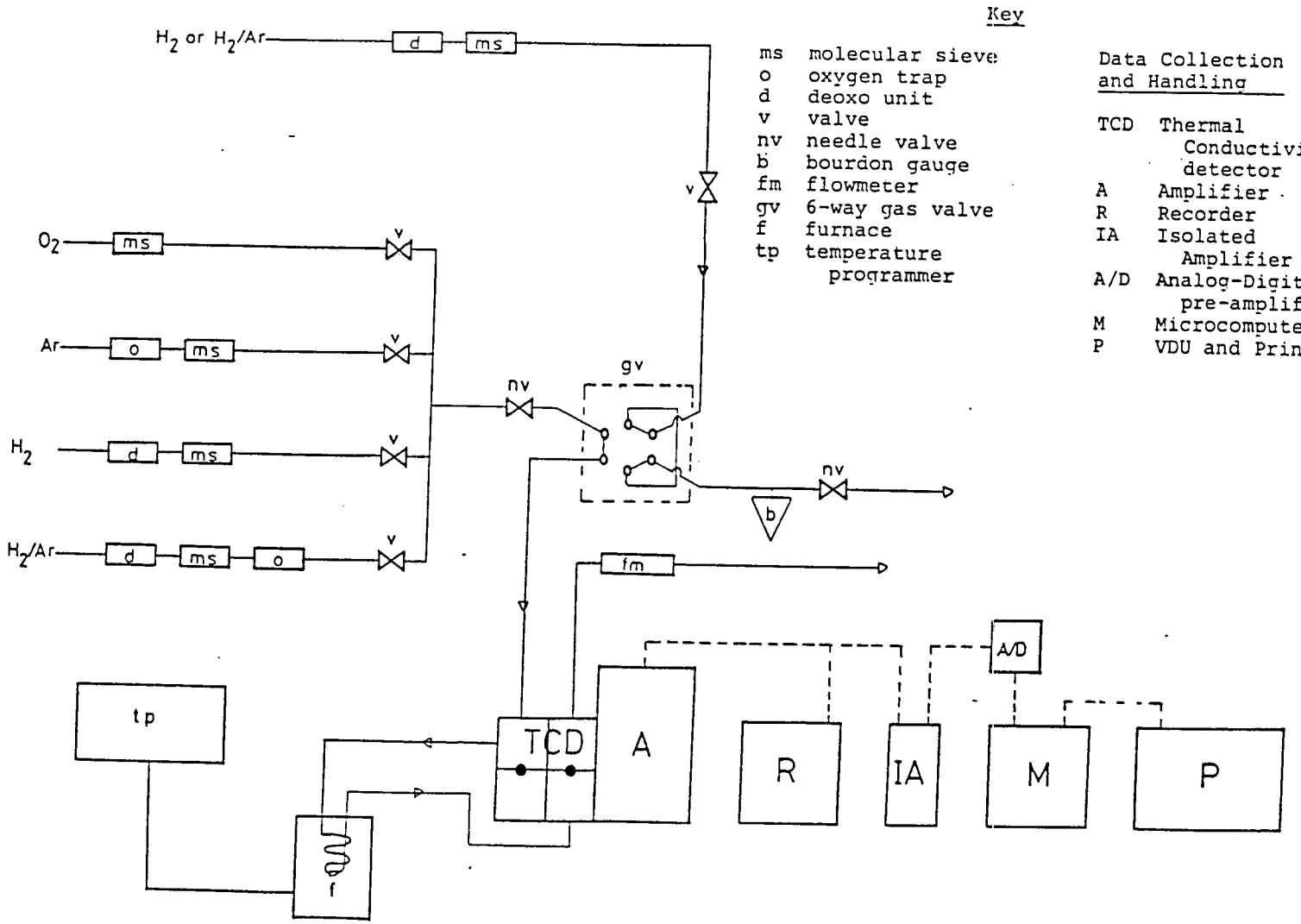


Figure 4.1 Line diagram of TPR/TPD system

catalyst bed. The gas flow rate was controlled by a Brooks Flow Controller (model 8744) and the 'normal' rate employed of 10 cm^3 min^{-1} was measured by a soap bubble meter.

The system was calibrated using hydrogen pulses and a Pt/SiO_2 catalyst, EUROPT-1[9,10].

4.2.3 Reduction Pretreatments

The characterisation of the catalysts and the hydrogenolysis experiments were carried out after the following pretreatments:-

LTR. The catalyst was reduced at 523K for 2 hrs in flowing hydrogen and evacuated at the same temperature for 0.5 hrs. In the flow system argon was used to degas the catalyst after reduction.

HTR. The catalyst, used in the previous experiment, was oxidised at 673K in flowing oxygen for 1 hr before cooling to room temperature in oxygen. The oxygen was replaced with hydrogen and the temperature raised to 773K. After 2 hrs reduction the catalyst was degassed for 0.5 hrs and cooled to the required temperature.

LTR-recovery (Regeneration). The same catalyst was again treated in oxygen as above and subjected to a LTR pretreatment.

4.2.4 Kinetic Experiments

Hydrogenolysis experiments were carried out on line 2

fitted with a static silica reaction vessel (volume = 1.77 x 10^{-6} m^3). The initial pressure of hydrocarbon was 0.945 KPa, *ca.* 3 x 10^{19} molecules, and hydrogen was used in a 10:1 excess. The analysis details have previously been given in section 3.2.3. Line 1, also fitted with a static reaction vessel (volume = 2.64 x 10^{-6} m^3), was used for the exchange experiments with the initial charge of hydrocarbon being 1.070 KPa. such a charge corresponded to approximately 7 x 10^{19} molecules of hydrocarbon and deuterium was present in 10:1 excess. The isotopic analysis was made with an operating voltage of 15 eV on the mass spectrometer to minimise fragmentation.

A more detailed description of the apparatus, experimental procedure and data handling was given previously in chapter 3.

4.3 RESULTS

4.3.1 Temperature-Programmed Reduction

Pt/TiO_2. The TPR profiles of differently treated Pt/TiO_2 samples are presented in figure 4.2. They all have similar characteristics of a low temperature reduction below 400K which occurs in two stages, followed by a small amount of hydrogen desorption. This phenomenon has been observed previously on Pt/SiO_2[11], Ir/Al_2O_3[12] and Rh/TiO_2 catalysts[5]. Reduction is also observed above 500K which continues into the isothermal period at 773K. The figures quoted within the curves are the calculated

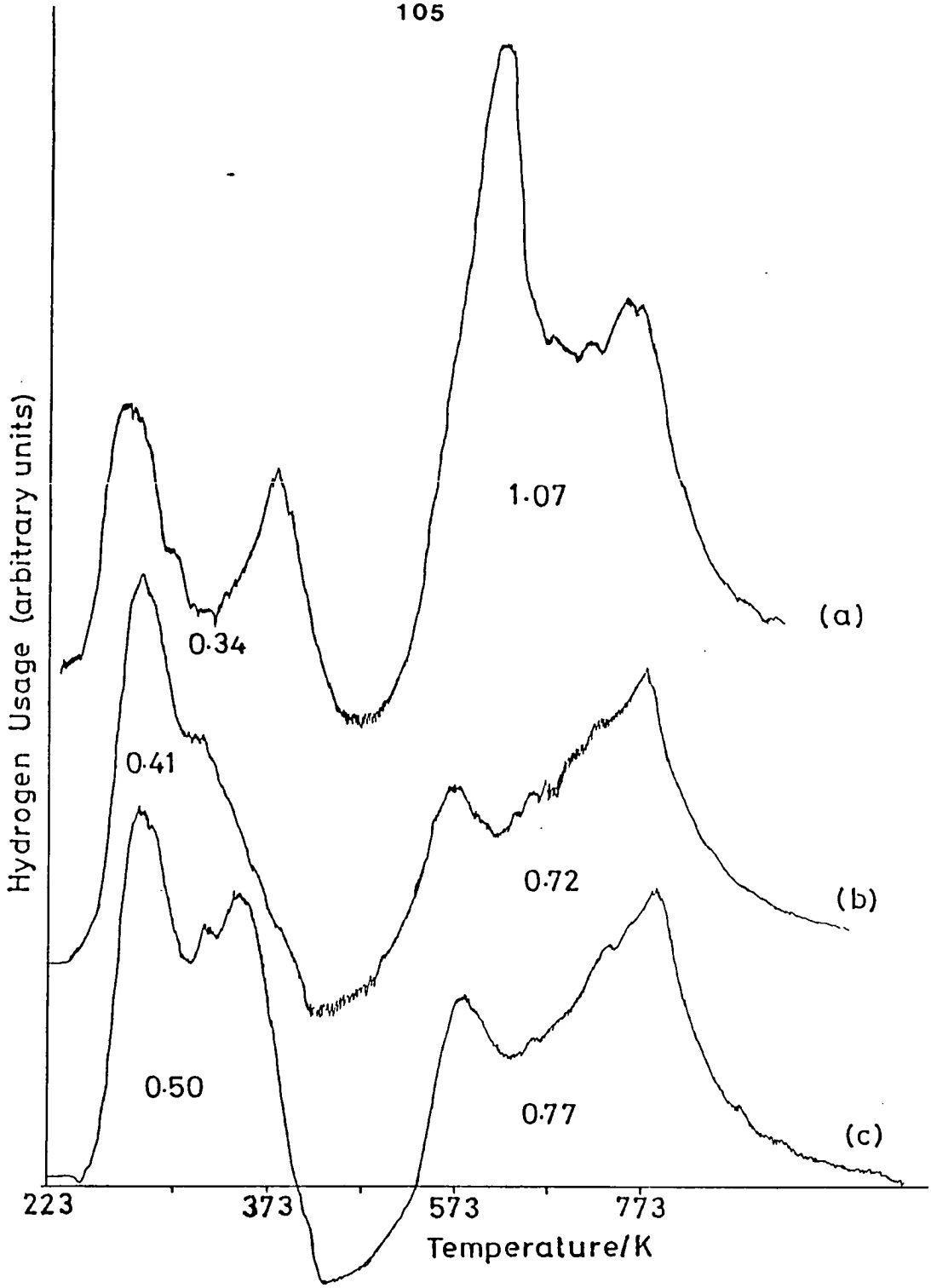


Figure 4.2 TPR profiles of Pt/TiO_2

(a) Untreated sample

(b) Sample (a) after reduction at 773K (2 hrs) and oxidation at 673K (1 hr)

(c) Sample reduced at 523K (2 hrs) and oxidised at 673K (1 hr).

amounts of hydrogen usage and are expressed as the amount of dihydrogen consumed per metal atom, i.e. H_2/M. The values for the low temperature peaks have been corrected for the amount of hydrogen desorption which precedes the high temperature peak.

The temperatures at which the rate of reduction is a maximum, T_{max}, for the low temperature region of the untreated sample, profile (a) in figure 4.2, are 261K and 391K. The first maximum is present in the other two spectra with little variation in T_{max}. The second maximum, however, is absent in profile (b) and occurs at 349K in profile (c). The high temperature regions of profiles (b) and (c) are very similar in their H_2/M and T_{max} values, but in profile (a) a large peak at 625K is also evident.

Pt/Nb_2O_5. TPR profiles of the niobia-supported platinum are presented in figure 4.3. The profile of the untreated sample, profile (a), is quite different from the freshly reduced and oxidised sample, profile (b), as are the H_2/M values. The high temperature reduction regions of the two samples have similar characteristics to those observed with Pt/TiO_2.

Rh/Nb_2O_5. No reduction below room temperature was observed for rhodium supported on silica or niobia, figure 4.4. The T_{max} of the silica-supported metal appeared at 360K, as previously reported[11], which was 20K higher than the less broad peak of the niobia-supported sample. There

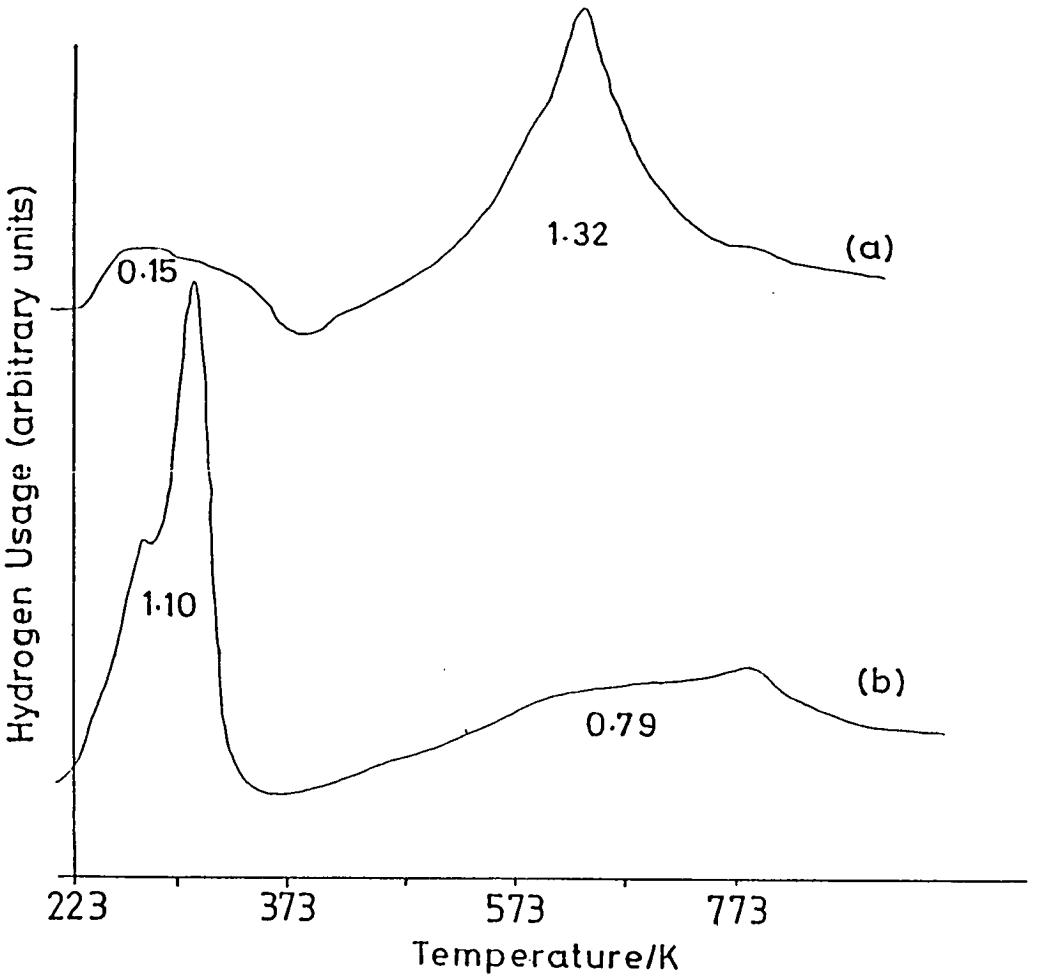


Figure 4.3 TPR profiles of Pt/Nb_2O_5

(a) Untreated sample.

(b) Sample (a) after reduction at 773K (2 hrs) and oxidation at 673K (1 hr).

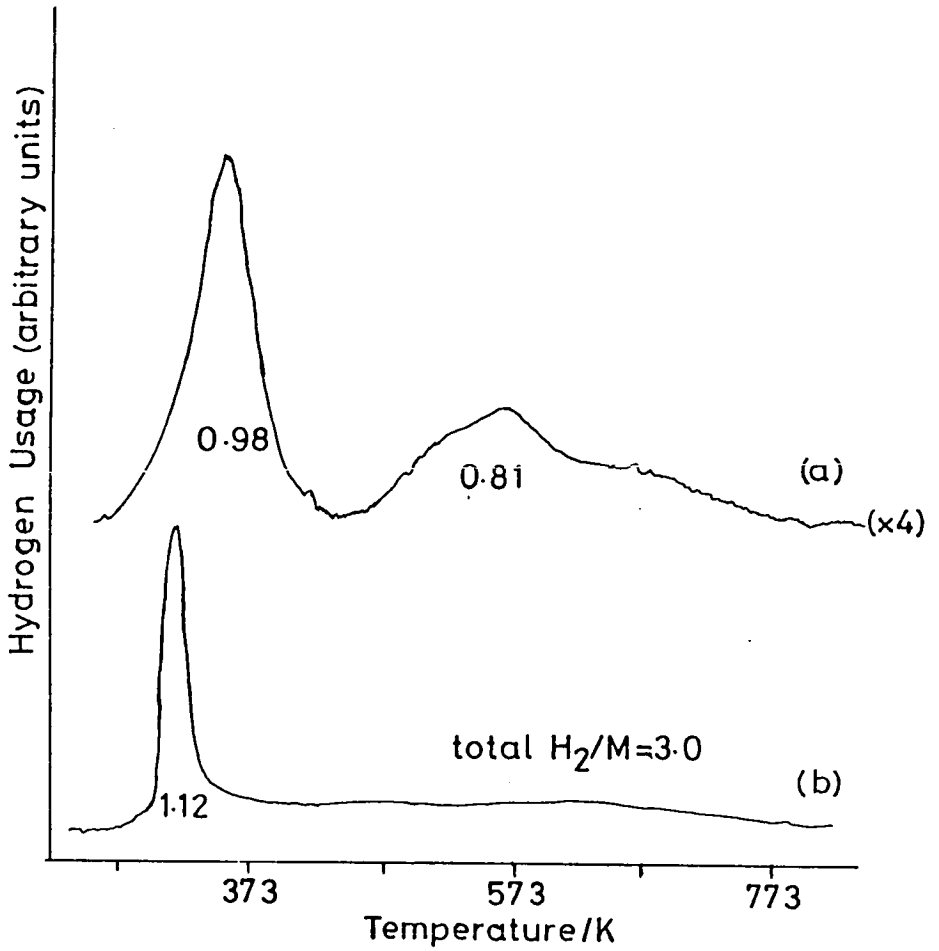


Figure 4.4 TPR profiles of

(a) Rh/SiO_2, and

(b) Untreated Rh/Nb_2O_5.

was little evidence of desorption after this peak especially with the Rh/Nb_2O_5 sample which exhibited a small amount of reduction until the maximum temperature of 773K was reached. The Rh/SiO_2 sample had a small high temperature peak at approximately 600K which had previously been attributed to either metal interacting strongly with the support or to some change in the support catalysed by the reduced metal[1].

Temperature-programmed reductions of the bare niobia and titania supports indicated that no detectable reduction occurred at temperatures below 700K.

4.3.2 Dispersion Measurements

Results of the dispersion measurements proved to be inconclusive. Due to the small metal loading, 1% w/w, and apparent low dispersion of these catalysts there was no measurable uptake of hydrogen from the injected pulses by the supported Pt catalysts. However, the measured amounts of hydrogen desorbed from the catalysts during TPD proved to be greater than that required to saturate the metal surface. This was the case for the three pretreatments. However, there were some obvious differences between the desorption spectra. Those from LTR catalysts exhibited a low temperature desorption region before the bulk of the measured hydrogen desorption occurred, whereas in the spectra from HTR samples such a region was either less pronounced or completely absent.

Table 4.1

Results from Dispersion Measurements for the Supported Metal Catalysts

Pretreatment	Pt/TiO_2 H/M[a]	Pt/TiO_2 total H_2[b] desorbed	Pt/Nb_2O_5 H/M[a]	Pt/Nb_2O_5 total H_2[b] desorbed	Rh/Nb_2O_5 H/M[a]	Rh/Nb_2O_5 total H_2[b] desorbed
LTR	0.07(0.12)[c]	0.95	0.30(0.18)[c]	-	0.04(0.10)[d]	0.91
HTR	0.05	1.23	<0.02	1.10	<0.02(0.04)[d]	1.03
Recovery	0.03	1.95	0.05	0.90	0.04(0.19)[d]	0.92

a. H/M dispersion based on one H atom per metal atom.
b. expressed as ratio of number of moles hydrogen desorbed to number of moles of metal present.
c. H/M values derived from desorption troughs during TPR.
d. H/M values derived from pulse chemisorption method.

Consequently, wherever it was possible dispersions were evaluated from the low temperature region of the desorption spectra, table 4.1, although for the supported rhodium catalyst results are also given from the pulse method.

4.3.3 Hydrogenolysis Experiments

Pt/TiO_2

LTR. 2-Methylbutane hydrogenolysis was investigated in the temperature range of 450-524K. The reactions were well behaved with the rate of loss of reactant linear with time and single bond rupture being the dominant process, table 4.2. At the highest temperature used however there was some evidence of isomerisation to n-pentane but, as figure 4.5 indicates, this only rose to a maximum of 2%. It was evident from the initial product distribution curves that as the isomerisation product goes through a maximum, the amounts of ethane and propane also increased with time. As these are the expected products from the hydrogenolysis of n-pentane this molecule is obviously competing successfully against 2-methylbutane for the surface. There was no visible downward trend of n-butane over the duration of the experiments to suggest that this product was reacting also.

HTR. The catalysts displayed low activity after HTR and consequently the reaction rates (conveniently measured in the temperature range 493K-623K) and initial product

Table 4.2

2-Methylbutane Hydrogenolysis over Pt/TiO_2

	T/K	10^4r/molecule s^{-1}(Pt atom)$^{-1}$	Initial Product Distribution						
			S_1	S_2	S_3	S_4'	S_4	S_5	M_b
LTR	473[a]	0.91	0.97	0.02	0.03	0.75	0.25	-	1.02
	498	1.53	0.99	0.03	0.04	0.67	0.30	-	1.03
	498	1.76	0.92	0.04	0.04	0.68	0.28	-	0.96
	524	3.39	0.82	0.07	0.08	0.52	0.27	0.13	1.02
HTR	593	1.38	3.94	0.07	0.04	0.13	0.07	-	3.25
	622	2.72	1.31	0.13	0.12	0.32	0.18	0.17	1.48
	623	2.02	2.66	0.11	0.08	0.17	0.10	0.13	2.59
Recovery	473	0.43	(1.34)[b]	-	-	(0.64)[b]	(0.28)[b]	-	(1.26)[b]
	526	3.40	1.28	0.07	0.06	0.46	0.27	0.07	1.30

a. an experiment using n-pentane at this temperature gave a rate of 0.53×10^{-4} molecule s^{-1}(Pt atom)$^{-1}$.

b. these figures are less accurate.

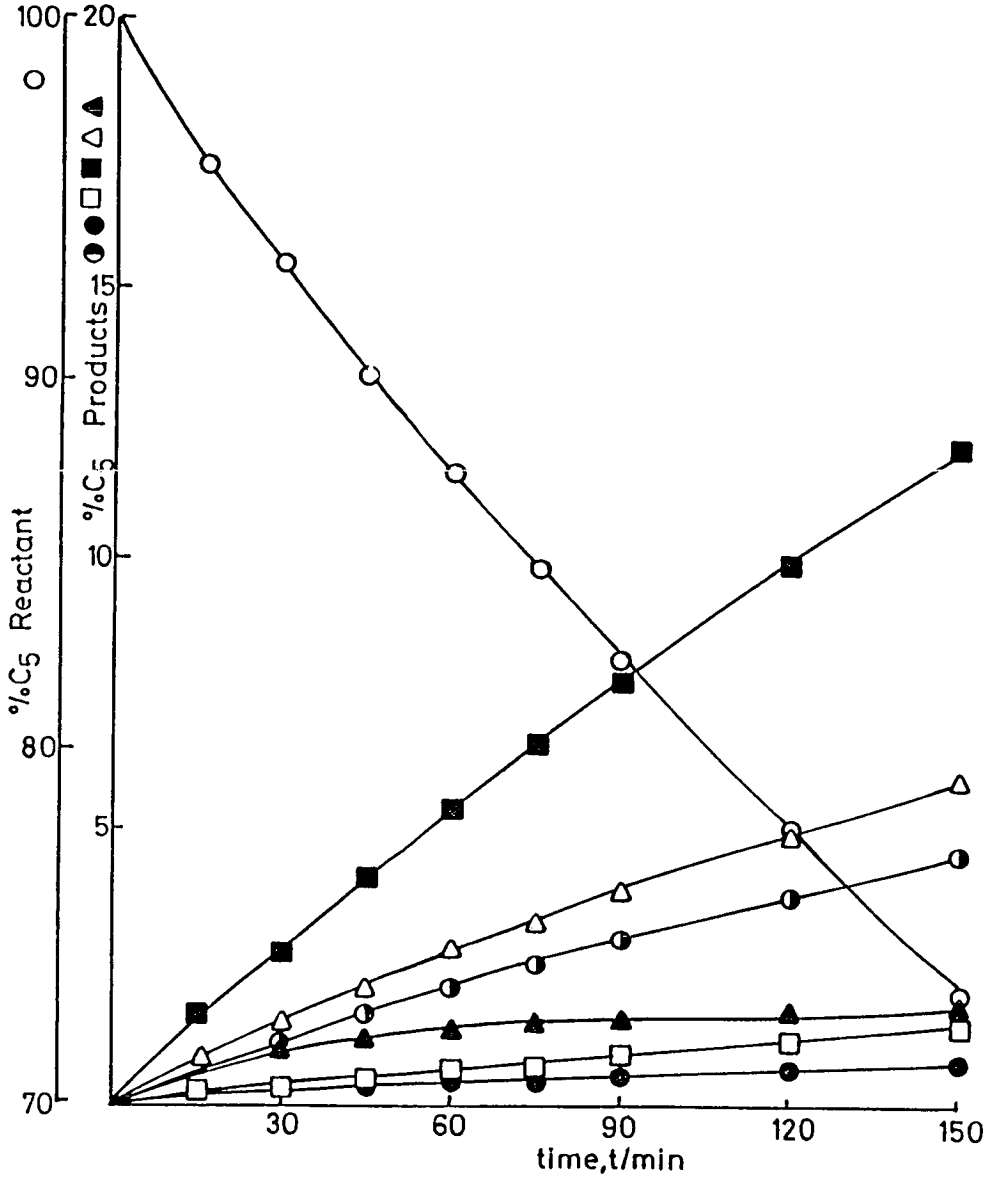


Figure 4.5 Reaction profile of 2-methylbutane hydrogenolysis over Pt/TiO_2 at 524K:

◐, methane; ●, ethane; □, propane;
■, 2-methylpropane; △, n-butane;
▲, n-pentane; ○, 2-methylbutane.

distributions were somewhat variable. However, in all cases it was clear that some multiple bond rupture had occurred, table 4.2. At 623K n-pentane was formed to a greater extent than at 524K over the LTR catalyst. As the production of C_2H_6 and C_3H_8 was observed to be linear with the amount of 2-methylbutane reacted, it was assumed that the n-pentane product did not significantly compete for the surface.

Regeneration. Although the activity of the LTR catalyst was regained after regeneration, table 4.2, there was some evidence of enhanced multiple bond rupture and a reduced isomerisation to n-pentane, i.e 7% as opposed to 13%.

Pt/Nb_2O_5

LTR. Hydrogenolysis experiments over this catalyst were carried out in the temperature range of 447K to 523K. The reactions were well behaved over the complete temperature range and although there was only 2% conversion at the lowest reaction temperature, initial product distributions were readily obtained, table 4.3. The low temperature reactions were required to ensure that the reaction was studied over an adequate temperature range because there was some evidence from the Arrhenius plot, figure 4.6, that at the higher temperatures the formation of n-pentane was interfering with the reactant. An activation energy of 87±7 $kJmol^{-1}$ was derived from the Arrhenius plot when these reactions were excluded, which

Table 4.3

2-Methylbutane Hydrogenolysis over Pt/Nb_2O_5

	T/K	10^4r/molecule s^{-1}(Pt atom)$^{-1}$	Initial Product Distribution S_1	S_2	S_3	S_4'	S_4	S_5	M_b
LTR	447	0.08	0.94	0.03	0.03	0.61	0.34	-	0.95
	447	0.13	0.95	0.07	0.04	0.63	0.36	-	1.05
	473	0.45	0.91	0.04	0.05	0.60	0.37	-	0.97
	474	0.43	0.95	0.04	0.05	0.60	0.36	-	1.00
	497	2.03	0.90	0.08	0.09	0.49	0.41	-	0.97
	498	2.21	0.90	0.09	0.10	0.49	0.41	-	1.00
	523	2.69	0.88	0.10	0.11	0.51	0.41	trace	1.01
	524	3.54	0.81	0.09	0.11	0.43	0.36	0.10	1.00
HTR	573	0.03	not measured						-
	573[a]	0.01(3)[a]	see footnote [a]						
Recovery	449	0.10	0.93	0.05	0.03	0.59	0.38	-	0.98
	473	0.61	0.90	0.05	0.06	0.54	0.40	-	0.95

a. Reaction using n-pentane; initial product distribution S_1=0.69; S_4=0.11; S_5'=0.80.

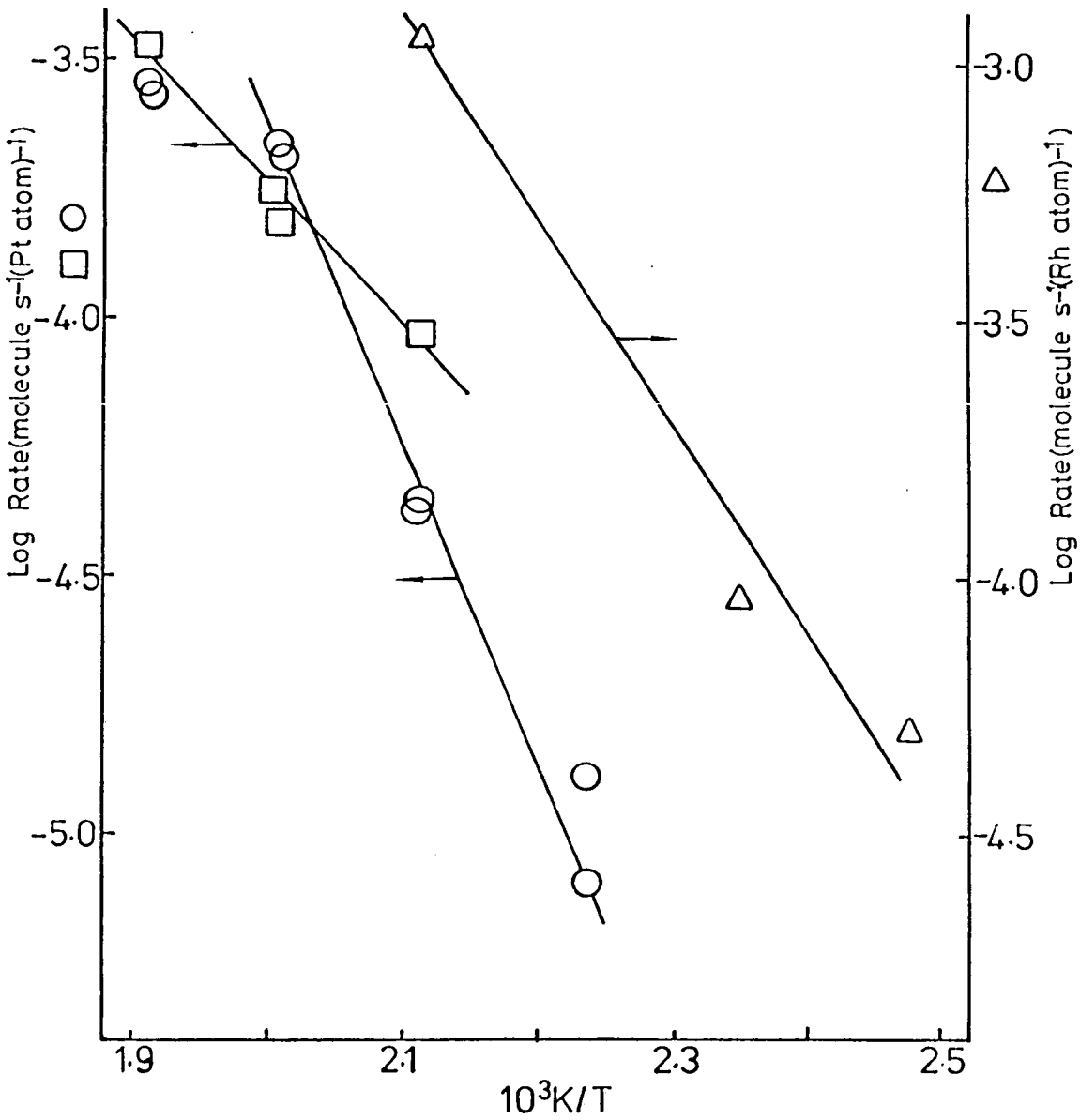


Figure 4.6 Arrhenius plots for 2-methylbutane hydrogenolysis over Pt/TiO_2 (□), Pt/Nb_2O_5(○), and Rh/Nb_2O_5(△).

can be compared to a value of 72±7 $kJmol^{-1}$ for the same reaction over Pt/TiO_2. Single bond rupture was againprominent over the full temperature range studied.

HTR. The results of experiments over HTR samples were complicated by the production of about 0.1% of 2-methylbut-2-ene. At 573K the equilibrium amount of 2-methylbut-2-ene expected under the reaction conditions used would be 0.26%. The sum of all other products totalled less than 0.1%. An experiment with n-pentane as the reactant was well behaved, figure 4.7. The initial rate was 2.5 times lower than that reported for 2-methylbutane but the formation of products was not complicated by any dehydrogenation reactions, table 4.3, even though the main product was 2-methylbutane.

If the initial rate of the 2-methylbutane reaction over the HTR sample is assumed to be 0.02×10^{-4} molecules s^{-1} $(Pt\ atom)^{-1}$ at 573K then extrapolation of the hydrogenolysis rate over LTR catalysts using the determined activation energy implied that the hydrogenolysis rate is suppressed by a factor of 6×10^2. A similar extrapolation for Pt/TiO_2 gave a suppression factor of 10 at 593K.

Regeneration. Re-reduction of a sample at 523K which had previously been reduced at 773K and oxidised at 673K generated a catalyst with the same activities and selectivities as a freshly reduced sample, table 4.3.

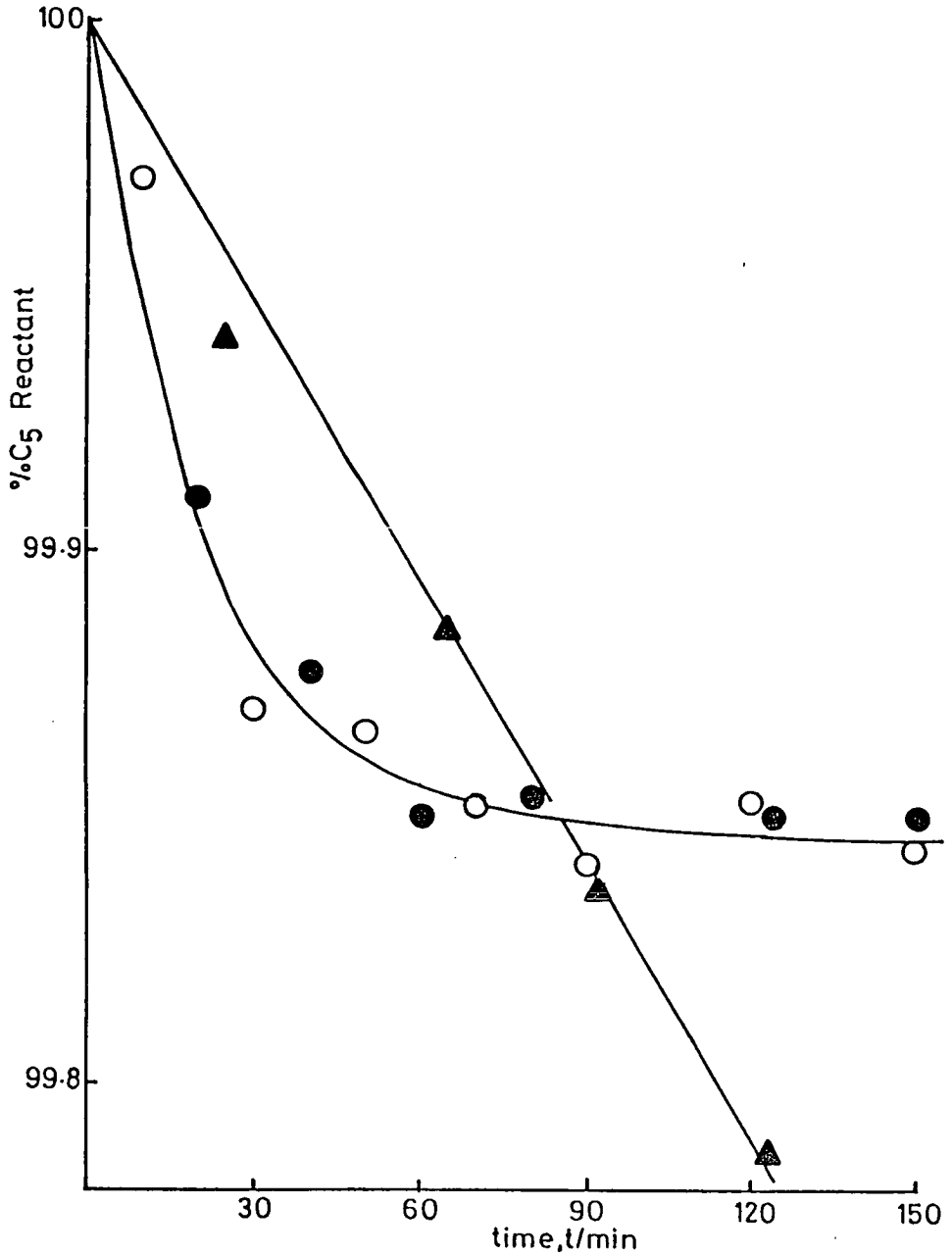


Figure 4.7 Hydrogenolysis reactions over HTR Pt/Nb_2O_5 at 573K:
●, ○, 2-methylbutane; △, n-pentane.

Rh/Nb_2O_5

LTR. The hydrogenolysis of 2-methylbutane was studied at temperatures of 404K, 426K and 473K. The reaction profile of the highest temperature is shown in figure 4.8. Normal pentane was formed at all three temperatures but its effect on the reaction of the main reactant is most clearly observed at the highest temperature. At this temperature the maximum amount of n-pentane formed was only 0.6%, a figure far removed from the expected thermodynamic equilibrium of 15.8%, but even this small amount competed successfully with the 2-methylbutane for the active surface. This is obvious not only from the downward trend of the amount of n-pentane, but also from the production of considerable amounts of ethane and propane. The initial product distribution plot, figure 4.9, shows such behaviour very clearly. The amount of n-butane formed also decreased which suggests that this smaller molecule also competes for the surface. Initial product distributions and the derived rates of reaction are given in table 4.4. The rate data are also given in the form of an Arrhenius plot, figure 4.6, from which an activation energy of 74±8 $kJmol^{-1}$ was obtained.

HTR. Two experiments carried out over a HTR sample gave similar, very low, initial rates, the amount of reaction being approximately linear to 0.3% after 2.5 hrs. The main products were methane and n-pentane but due to the complexity of the surface reactions occurring an

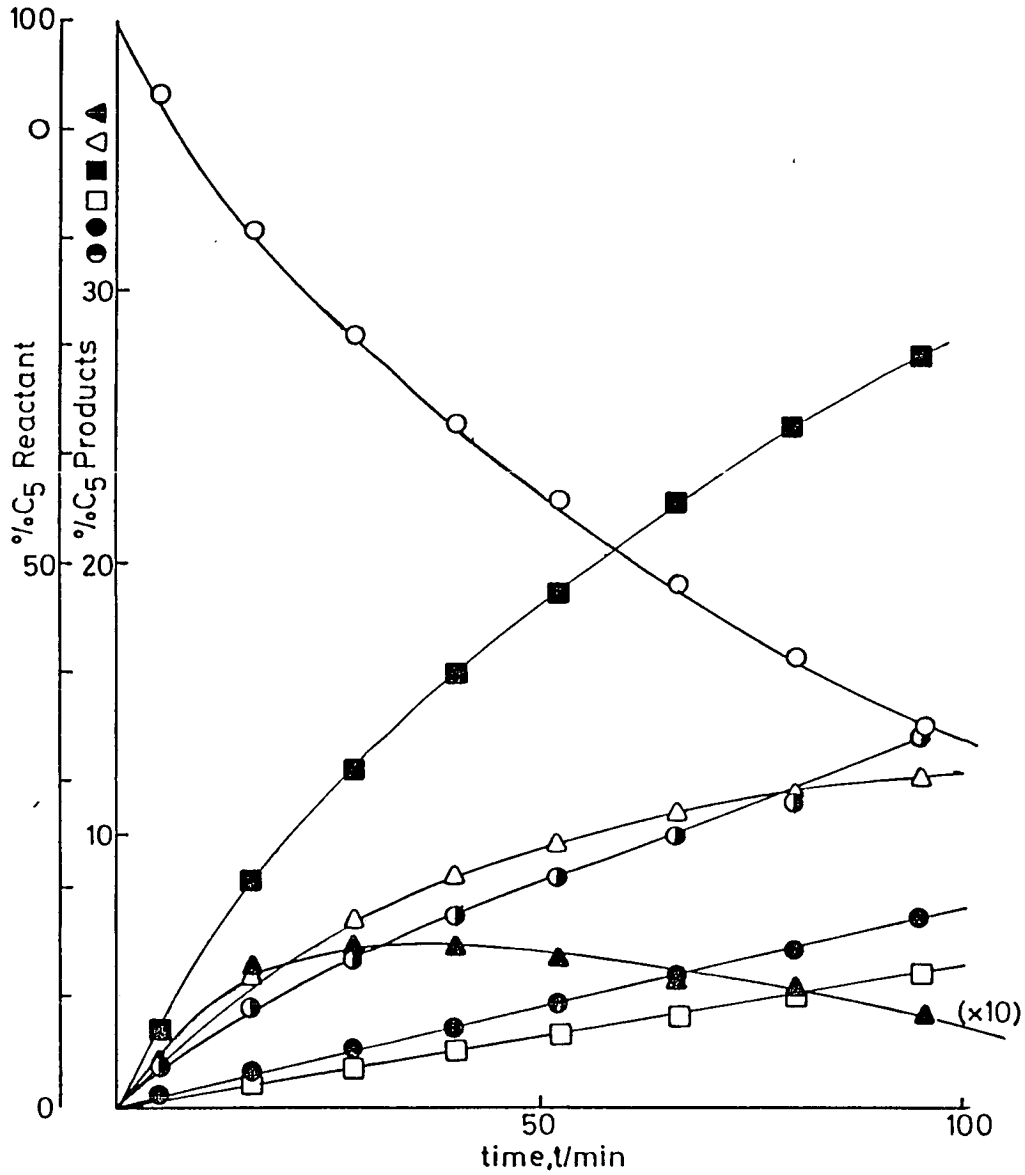


Figure 4.8 Reaction profile of 2-methylbutane hydrogenolysis over Rh/Nb_2O_5 at 473K:
◑, methane; ●, ethane; □, propane;
■, 2-methylpropane; △, n-butane;
▲, n-pentane; ○, 2-methylbutane.

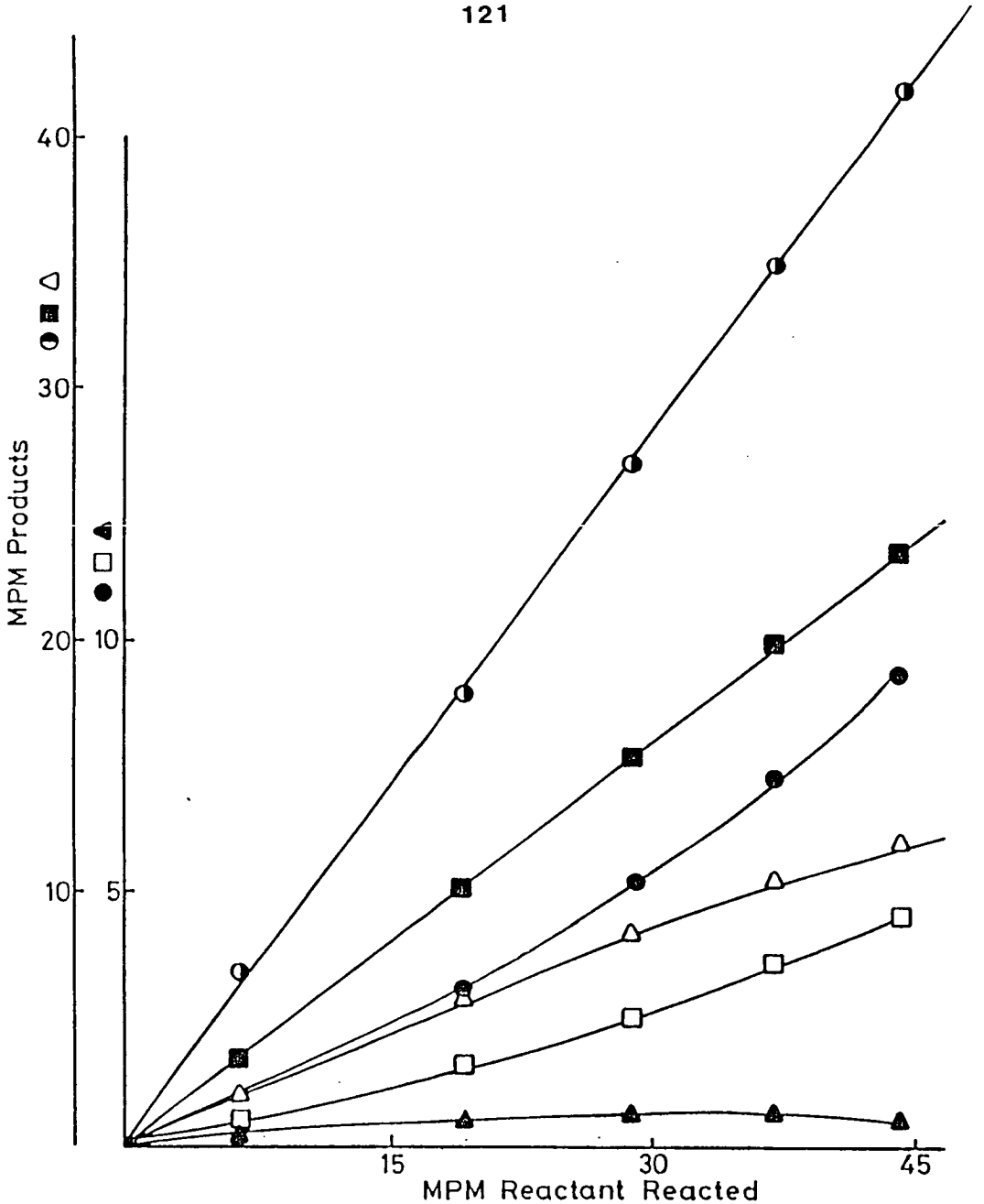


Figure 4.9 Distribution of initial products from 2-methylbutane hydrogenolysis over Rh/Nb_2O_5 at 473K:

◑, methane; ●, ethane; □, propane;

■, 2-methylpropane; △, n-butane;

▲, n-pentane.

Table 4.4

2-Methylbutane and n-Pentane Hydrogenolysis over Rh/Nb_2O_5

	T/K	10^4r/molecule s^{-1}(Pt atom)$^{-1}$	Initial Product Distribution							
			S_1	S_2	S_3	S_4'	S_4	S_5'	S_5	M_b
LTR	404	0.5	0.93	0.08	0.05	0.62	0.29	-	0.03	1.03
	426	0.9	0.93	0.07	0.05	0.57	0.33	-	0.03	1.01
	473	10.9	0.95	0.16	0.08	0.53	0.30	-	0.03	1.08
HTR	572	0.007	not measured							
	573	0.010	not measured							
Recovery	473	11.1	0.95	0.15	0.07	0.55	0.31	-	0.03	1.09
n-Pentane										
LTR	423	2.0	0.23	0.80	0.79	-	0.18	0.02	-	1.04
HTR	571	0.017	0.57	0.08	0.08	-	0.20	0.65	-	1.66
Recovery	423	2.0	0.19	0.82	0.82	-	0.15	0.02	-	1.02

initial product distribution could not be obtained. Using the activation energy for the LTR catalysts and extrapolating to the reaction temperature of 573K, it was found that 2-methylbutane hydrogenolysis is suppressed by a factor of 10^5 over HTR samples.

An investigation of n-pentane hydrogenolysis over LTR and HTR Rh/Nb_2O_5 at 423K and 571K respectively showed that at both temperatures the linear hydrocarbon reacted at about twice the rate of the branched alkane, table 4.4. Over the LTR catalyst single bond rupture was the main reaction with central bond fission predominating. In contrast with 2-methylbutane the linear hydrocarbon exhibited no complications over the HTR sample and an initial product distribution, table 4.4, indicated that isomerisation and multiple hydrogenolysis both took place.

Regeneration. The oxidation treatment of an HTR sample (at ~673K) resulted in the restoration of the activity and the selectivity of the catalyst to the original values - see table 4.4.

4.3.4 2-Methylbutane Exchange over Pt/Nb_2O_5

LTR. The rate of exchange of 2-methylbutane was studied over the temperature range 298K to 355K. At the lowest temperature the reaction was well behaved, obeying the first-order rate equations discussed in section 3.4.2, but at the highest temperature the exchange rate was relatively fast with diffusion control possibly becoming

significant. The initial product distribution determined for this experiment, table 4.5, should also be viewed with caution. An activation energy of 45±3 $kJmol^{-1}$ was obtained for the exchange reaction over the LTR catalysts. The initial product distributions for the LTR catalysts, table 4.5, indicate that at low temperatures moderate amounts of d_1 are produced with a spread of small amounts of highly-deuterated molecules including a small maximum for the perdeuteromolecule. With an increase in temperature the amount of d_1-product diminished with a subsequent increase in the highly deuterated species.

Also given in table 4.5 for comparison is the initial product distribution obtained from 2-methylbutane exchange over a Pt/SiO_2 catalyst at 333K. Although this experiment was carried out under slightly different conditions, the initial product distribution, as well as the rate of exchange, is very similar to those of the Pt/Nb_2O_5 catalyst.

HTR. The exchange of 2-methylbutane with deuterium over HTR Pt/Nb_2O_5 proved to be demanding and required temperatures in excess of 543K; at such temperatures reproducibility was relatively poor. At elevated temperatures alkene was formed - such formation may have been responsible for observed reaction rates being lower than those noted at 543K. This latter experiment was well behaved, again obeying the first-order rate equations, section 3.4.2, allowing a rate and initial product

Table 4.5

2-Methylbutane Exchange over Pt/Nb_2O_5

	T/K	10^4r/molecule s^{-1}(Pt atom)$^{-1}$	Initial Product Distribution D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}	D_{11}	D_{12}	M
	298	8.31	0.43	0.12	0.06	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.08	4.0
	298	6.64	0.48	0.11	0.06	0.05	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.09	3.7
LTR	315	23.26	0.39	0.11	0.06	0.05	0.04	0.03	0.03	0.03	0.04	0.04	0.06	0.12	4.6
	355	144.5	0.16	0.08	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.06	0.09	0.17	7.7
	333[a]	21.59	0.42	0.12	0.06	0.05	0.04	0.03	0.03	0.03	0.04	0.04	0.04	0.09	4.2
HTR	543	8.31	0.11	0.05	0.03	0.02	0.02	0.02	0.03	0.05	0.08	0.09	0.20	0.31	8.7
Recovery	298	11.63	0.42	0.12	0.07	0.04	0.04	0.02	0.02	0.02	0.04	0.04	0.05	0.11	4.0

a. Pt/SiO_2 catalyst

distribution to be determined, table 4.5. As this rate was particularly reliable it was used to calculate a lower limit for the degree of suppression of the exchange reaction caused by HTR. It was assumed that the activation energy determined for the exchange reaction over the LTR catalysts remained constant up to 543K and that no poisoning of the reaction occurred; the calculated suppression factor was 10^4.

The observed amount of alkene produced at 572K was estimated to be 0.28%, i.e. close to the calculated equilibrium amount of 0.29%. The amount of alkene produced was calculated from the mass spectrum using the peak heights at m/e 77 to m/e 80 corresponding to heavily exchanged alkene which would be produced at this temperature. The parent peak of the alkene was 8 times more sensitive than that of the alkane under the conditions used which allowed the small amounts of alkene produced to be easily identified. Also, if the remaining peaks at m/e 73 to m/e 76, and m/e 81 to m/e 84 are assigned to lightly and heavily exchanged 2-methylbutane (m/e = 72) respectively, and the appropriate isotope and fragmentation corrections made, a reaction profile depicting the production of these three species can be produced, figure 4.10. The amount of highly exchanged alkane is increasing at a much faster rate than the 'alkene' which suggests that the multiple exchange reaction of the alkane is not a consequence of the

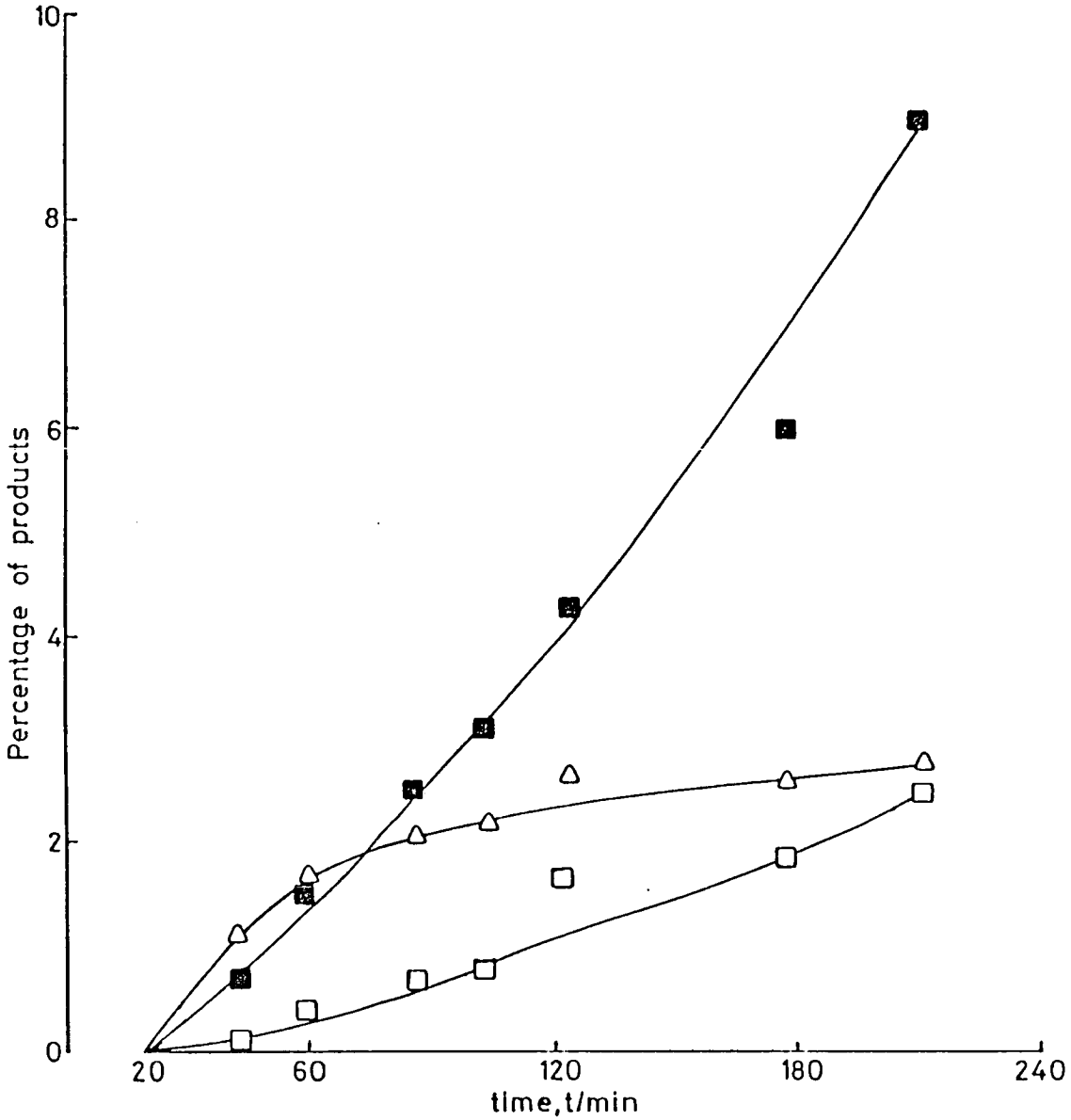


Figure 4.10 Results for 2-methylbutane exchange over HTR Pt/Nb_2O_5. Reaction temperature increased from 543K to 572K after 20 mins:
□, lightly exchanged alkane (m/e 75 to 78 incl.); ■, heavily exchanged alkane (m/e 83 to 86 incl.); Δ, alkene (m/e 79 to 82 incl.).

production of the dehydrogenated species.

Regeneration. The reaction rates obtained from regenerated samples were also linear with time but the calculated rates showed some variation - a factor of 2 to 3 times different from the freshly reduced samples. The initial product distributions of the regenerated catalysts showed only slight differences from those determined for the LTR catalysts, table 4.5, but these are not conclusive evidence that the active sites have been affected by the treatment of the catalyst.

4.4 DISCUSSION

4.4.1 Characterisation

Although TPR is primarily a technique to monitor the reduction of a metal precursor it cannot in itself be totally isolated from other processes which may occur simultaneously. One of the more obvious processes is hydrogen adsorption by the reduced metal from the gaseous environment with subsequent desorption of this hydrogen at higher temperatures in the flowing hydrogen-containing carrier gas. This adsorption/desorption process is an inherent property of the reduced metal and is unavoidable. Thus the amounts of dihydrogen usage quoted in the TPR profiles of the low temperature peaks in figures 4.2 and 4.3, corrected for the subsequent hydrogen desorption troughs, should be considered to be minimum values.

Temperature-programmed reduction studies of

EUROPT-1[13,14], a well characterised Pt/SiO_2 catalyst known to have metal particles of a narrow size distribution, 1 to 4 nm with the mean at 1.9 nm, displays a near symmetrical reduction peak with a T_{max} at approximately 330K. The two peaks, which are either side of this temperature, observed with the TPR profiles of the Pt/TiO_2 catalysts suggests that this sample consists of Pt particles of a more heterogeneous character. As the first step in the reduction process involves dissociation of hydrogen this step is facilitated if the two hydrogen adsorption sites are close to each other. It is known that larger particles of supported platinum reduce at lower temperatures than do smaller particles[15,16]. This implies that the peak with T_{max} at about 265K is due to reduction of larger particles than those responsible for the subsequent reduction peak. This peak, which is not present after HTR and reoxidation, appears at 390 and 350K with the untreated and LTR samples respectively.

Another difference between profiles (a) and (c) of figure 4.2 is the large peak at 625K which is also not present in profile (b). The increase in the H_2/M values of the low temperature peaks of profiles (b) and (c) suggest that this peak may be due to small platinum particles. When reduced such particles agglomerate to become larger Pt particles which subsequently display a lower reduction temperature. A similar feature is evident in the untreated Pt/Nb_2O_5 sample, profile (a) of figure

4.3. This also exhibits a peak with a T_{max} at 625K which after reduction, either at 523K or 773K, and reoxidation, is not present in the subsequent TPR. The H_2/M values of the treated catalysts indicate that the particles causing the large high temperature reduction peak agglomerate and then reduce at the values found for the low temperature peaks.

The smaller H_2/M values found for the Pt/TiO_2 samples suggest that not all the platinum was in a fully oxidised state and that most of the metal was present as Pt^o. Such a situation would also account for the lower temperatures of reduction if the particles consisted of a metallic core with an oxide skin[16]. The small hydrogen molecules can diffuse through the oxide layer and as long as metallic platinum is present, hydrogen will be dissociated and reduction will proceed without any inhibition. The larger H_2/M values found for the treated Pt/Nb_2O_5 catalysts indicate that the platinum present on these catalysts equates to PtO. It has been reported[15] that unsupported PtO reduces at 278K which is not too dissimilar from the T_{max} of 290K found for these samples. These peaks are sharper and appear at a lower T_{max} than that found for EUROPT-1[13,14] implying that the platinum particles although greater in size may have a smaller size distribution.

The high temperature reduction peaks of profiles (b) and (c) in figure 4.2 have a maxima at 565K, 710K and 765K

which are very similar to those found for a 4% Pt/TiO_2 catalyst[16], i.e. 573K, 713K and 873K. The authors attributed them to metal assisted reduction of the anatase support, and as no reduction was observed with the anatase support until temperatures >700K were reached the same conclusion is drawn here. The results are also consistent in that comparable amounts of hydrogen, $H_2/M = 0.7$, were recorded during this reduction. Similar values were found for the Pt/Nb_2O_5 catalysts, although there were no discernable peak maxima this could be a consequence of the lower sensitivity used for the collection of the data.

The TPR profile of the Rh/SiO_2 catalyst is included in figure 4.4 for comparison with the niobia-supported rhodium. Both catalysts have the same metal loading. The silica-supported sample had been investigated by a variety of experimental techniques and had led the researchers[11,17,18] to maintain that the metal was well dispersed on the support. The TPR profile shows that the bulk of the metal is reduced in the low temperature peak with a T_{max} at 360K, but reduction of more metal must occur in the high temperature peak, as well as some support, to account for the total hydrogen usage of 1.8. The shape of the low temperature peak would also suggest that the metal particles have a large size distribution with the smaller metal particles requiring a higher reduction temperature. In contrast the low temperature peak of the Rh/Nb_2O_5 catalysts is less broad and has a

lower T_{max} at 340K. This indicates particles that are larger but of a more uniform size. Temperature-programmed reduction studies of Rh catalysts with various metal-loadings on alumina and titania supports[5] showed that on the former, reduction of the metal oxide precursor occurred below 300K, and for the low loaded metal on the latter support reduction occurred between 330-340K. This is in excellent agreement with the present value of 340K found for the Rh/Nb_2O_5 sample. Further reduction of Rh/TiO_2 catalysts occurred with reported maxima at 600K and 740K[5]. This was attributed to reduction of the support in the near vicinity of the metal particles. This is believed to be also the case with the niobia-supported rhodium which although not exhibiting any maxima had a long reduction tail up to the maximum temperature. The H_2/M value of 3.0 is far in excess of the amount of hydrogen required to reduce just the metal and is evidence that metal induced reduction of the Nb_2O_5 support is also occurring. TPR experiments to characterise a niobia-promoted Rh/SiO_2 catalyst[19] indicated that the T_{max} for the unpromoted Rh/SiO_2 sample was 350K with no reduction occurring after 423K. However, with the niobia-promoted catalysts hydrogen usage was evident until 773K and this was attributed to reduction of a $RhNbO_4$ compound formed by oxidation of the sample at 673K.

Desorption of hydrogen taken up from the reducing gas stream by the reduced metal was visible in all the TPR

profiles of the supported Pt samples. It was not present in the Rh/Nb_2O_5 TPR profiles. The temperatures at which this occurred was dependent upon the character of the preceding reduction peak. With the titania support the reduction peak at 391K in figure 4.2(a) delays the desorption until approximately 435K and the broad desorption trough, reaching a minimum at 438±10K, continues until 523K. Whereas, for profiles (b) and (c) of figure 4.2, where the reduction peaks occur at lower temperatures, the desorption occurs between 408K and 495K, and 413K and 533K respectively. Both have a minimum at approximately 435±10K. This temperature agrees well with that reported from a similar phenomenon observed with EUROPT-1 of 480±20K[13]. Similarly with Pt/Nb_2O_5 samples, because of the preceding broad reduction peak, the desorption trough of profile (a) of figure 4.3 occurs between 361K and 443K, but with the treated samples desorption occurs from approximately 340K to 455K. The temperatures at which these troughs reach a minimum are lower than those for the Pt/TiO_2 samples, being 383K, 363K and 388K for profiles (a), (b) and (c) respectively. Measuring the amounts of hydrogen desorbed in these two supported catalysts gives H/M ratios of 0.12 for Pt/TiO_2 and 0.18 for Pt/Nb_2O_5. As previously mentioned, however, there is clearly an overlap between the process of reduction and hydrogen desorption, and so these figures must be considered to be minimum values.

Previous work with platinum supported on silica[11] had indicated that the amount of hydrogen desorbed during this period was similar to the hydrogen desorbed from a conventional TPD experiment. Although the agreement in the present study is not as conclusive due to the difficulties encountered in the TPD experiments, the results in table 4.1 however, do give a rough indication of the dispersion of these two Pt catalysts.

The difficulties described in the TPD experiments are not isolated phenomena. Of three hydrogen TPD states to have been observed on model Pt/TiO_2 catalysts[20-25] the highest temperature state was thought to represent hydrogen spilled-over onto the titania surface or into the bulk[24,25]. This state once formed would require either high temperatures or long periods of time before diffusion back to the metal; indeed there is some evidence that after reduction and evacuation, hydrogen migrates back to the surface of Pt/TiO_2 catalysts over periods of up to 16 hours[26]. Increasing the temperature of reduction shifts the desorption peaks of these spillover states to higher temperatures[20]. As the lower states of desorption were from the metal the desorption of hydrogen was suppressed by treatment at high temperature, but the total amount of hydrogen desorbed was approximately equal to that required to saturate the metal surface[20,24,26].

4.4.2 Kinetic Studies over LTR Catalysts

Before discussing the influence of metal-support interactions induced by high temperature reduction of the transition metal-oxide supported metals it is appropriate to explore the possibility that support effects may exist between the metals and oxide supports when they are in a 'normal state', i.e. having normal adsorption properties. There is now good evidence that titania-supported metals in a non-SMSI state may have unusual catalytic properties. For example, it is well established that normal titania-supported metals have a higher activity for the CO/H_2 reaction[27,28]. More recently it has also been shown that Rh/TiO_2 catalysts have a high activity for n-hexane conversion[29,30] and give quite different product distributions in the n-hexane[29] and methylcyclopentane[31] reactions. Similarly, it has been shown for the methylcyclopentane reaction that Pt/TiO_2 catalysts give quite different product distributions to Pt/SiO_2 catalysts[29]. None of these support effects are dependent on SMSI. It has also been demonstrated that the titania-supported metals, Pt and Rh, behave differently[32]. Platinum, for instance, enters the SMSI state much more easily than rhodium. It is also more difficult to recover the original adsorption capacity of the platinum metal.

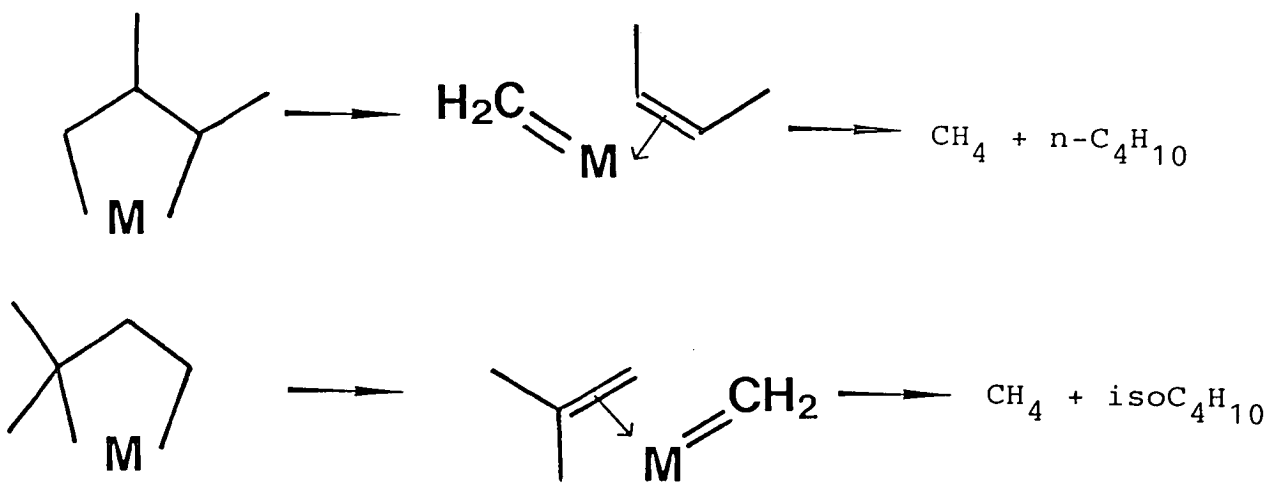
It is well documented that platinum is a good example of a metal where there is a strong tendency for only one C-C bond to be ruptured in any particular hydrocarbon[33].

Indeed it is recognised that in the hydrogenolysis of alkanes with a number of non-identical carbon-carbon bonds platinum tends to promote non-selective bond scission[34,35]. The present results from the titania- and niobia-supported platinum conform to the former statement, the M_b value for each catalyst being unity over the temperature range studied. However, the selectivities indicated preferred breaking of the bond between the primary and secondary carbons to give methane and 2-methylpropane as the major products. The amount of 2-methylpropane produced was approximately 2-3 times the amount of n-butane formed but the differences diminished with increase in temperature. This was particularly evident with the niobia-supported platinum catalyst. Isomerisation to n-pentane was only evident at the highest temperatures used for both platinum catalysts.

It is now generally accepted that hydrogenolysis proceeds via adsorbed hydrocarbon species formed by the loss of more than one hydrogen atom from the parent molecule and that in these adsorbed species more than one carbon atom is in some way involved in bonding to the catalyst surface.

Foger and Anderson have distinguished two types of hydrogenolysis modes on Ir catalysts, the C_2- and the iso-unit modes[36]. The former, which is the least activated process, can only occur with primary or secondary carbon atoms and requires larger ensemble sizes

than the latter process which requires only one active metal atom. This last process may also be accompanied by bond shift isomerisation proceeding via a C_3 carbocyclic intermediate[37]. Furthermore, 2,2-dimethylpropane, which can only form 1,3-adsorbed species, has the same activity as butane, 2-methylpropane and 2-methylbutane and is more reactive than ethane so it has been proposed that an important hydrogenolysis pathway is via 1,3-adsorption[38]. Thus demethylation of 2-methylbutane to give n-butane and 2-methylpropane may occur through the 1,3-adsorbed species as shown in scheme 4.1.

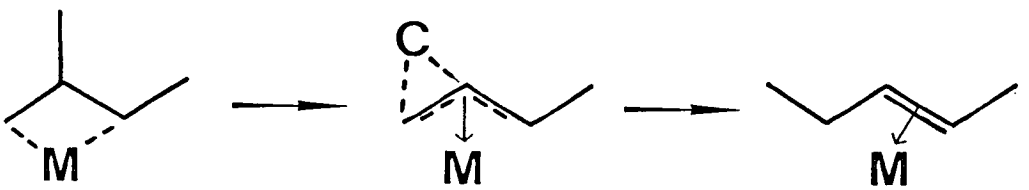


Scheme 4.1

Internal fission of 2-methylbutane has been reported to have a higher activation energy than demethylation[39]. A further study of Pt/Al_2O_3 catalysts has intimated that

the internal fission may be disfavoured because of the significant difference found in reactivity of bonds between primary and tertiary carbons and those between secondary and tertiary carbons[40]. In the latter case formation of an alkylidene species and an alkene would result.

The bond shift isomerisation of 2-methylbutane to n-pentane could also be explained by the formation of a metallocyclobutane[39], scheme 4.2.



Scheme 4.2

This mechanism has also been shown to require a higher activation energy than the demethylation reaction.

Comparison of the 2-methylbutane hydrogenolysis results over the platinum catalysts at 473K with those of previous studies over Pt/Al_2O_3[41] and Pt/SiO_2[18] using similar conditions is made in table 4.6. Differences in activity ranged over a factor of only 3, the more significant differences being between the initial product distribution of the Pt/SiO_2 catalyst and those of the

Table 4.6

2-Methylbutane Hydrogenolysis over Platinum Supported on Various Oxides at 473K

Support	H/M	10^4r/molecule s^{-1}(Pt atom)$^{-1}$	Initial Product Distribution						M_b	Ea/ kJmol^{-1}
			S_1	S_2	S_3	S_4	S_4	S_5		
SiO_2	0.98	1.46	0.79	0.16	0.15	0.40	0.36	0.09	1.04	130
Al_2O_3	1.21	0.71	0.96	0.04	0.04	0.64	0.32	-	1.00	-
TiO_2	0.10	0.91	0.97	0.02	0.03	0.75	0.25	-	1.02	72±7
Nb_2O_5	0.30	0.45	0.91	0.04	0.05	0.60	0.36	-	1.00	87±7

other three supported samples. The silica-supported platinum still favoured the demethylation reaction over internal fission but not the selectivity shown by the remaining three catalysts for the formation of 2-methylpropane by scission of the bond between the primary and secondary carbons. Internal bond fission was not an important reaction on these catalysts. As the variation cannot be attributed to crystallite size differences, both the alumina and silica supported catalysts having dispersions near unity, it does seem likely that there is a support effect because the titania and niobia supports in their "normal" state have similar properties to the alumina. The bifunctional properties of alumina as a support are well documented and a review of the catalytic properties of pure alumina shows how diverse these can be[42]. The surface properties of TiO_2 have been reviewed[43,44] and more recent work[45] has confirmed the relatively limited catalytic properties of this oxide[46], although it is perceived to have both acidic and basic properties. Niobia is known to be strongly acidic when calcined at low temperatures but at high temperatures, i.e. >773K, it does not exhibit any acidic properties. Indeed it has been found that calcination at temperatures in excess of 673K promotes crystallisation to the T-T phase of Nb_2O_5 - the crystallisation being complete at 973K[3,47]. Catalytic studies of but-1-ene[3] and 3,3-dimethylbut-1-ene isomerisation[48] have shown that the

full activity of a sample pretreated at 573K was completely restored by rehydroxylation whereas only partial restoration was possible from a sample heated at 773K. The transformation of the oxide from amorphous to its T-T phase was thought to make the regeneration of Brönsted acidity by treatment with water more difficult. Dehydration of butan-2-ol[3] indicated that at low pretreatment temperatures the main active sites were Brönsted acid type, but at higher evacuation temperatures Lewis acidity became predominant. Thus even in their "normal" states the TiO_2 and Nb_2O_5 supports affected the catalytic properties of the supported metal.

The possibility that residual Cl^- ions from the metal precursor may interfere with SMSI studies has been raised[49,50,51] and cannot be excluded from the current studies entirely as no analysis measurements of the type described have been made. However, chloride is generally considered to be a catalyst poison and the result of the niobia- and titania-supported platinum for 2-methylbutane hydrogenolysis are in close agreement with the alumina-supported sample, table 4.6. This latter catalyst was prepared using the metal acetylacetano complex[52].

The calculated activation energies for the 2-methylbutane hydrogenolysis reaction over the TiO_2- and Nb_2O_5-supported platinum are of similar magnitude and appreciably lower than that found for the same reaction over the silica-supported platinum, table 4.6. This is

probably due to the large differences in dispersion as it has been unequivocally shown[39] that on Pt/Al_2O_3 catalysts activation energies of all the reactions on pentanes, hydrogenolysis, bond shift and cyclic type isomerisation are higher on highly dispersed than on low dispersed catalysts.

Whereas, in reactions with alkanes, platinum is well known for its poor hydrogenolysis and high selectivity for isomerisation products, rhodium has been shown to be the most active metal, apart from ruthenium, for hydrogenolysis reactions involving ethane or heptane[33]. The high activity for bond scission displayed by rhodium is confirmed in the present study with niobia-supported rhodium being, at 473K, 20 times more active than its platinum counterpart for 2-methylbutane hydrogenolysis. This factor is not as large as that reported for the silica-supported metals, i.e. 365 times at 398K[18] but in that case the catalysts were well dispersed and on a non-interacting support. It has been argued in the literature[52,53] that a specific property of rhodium at high dispersion is its ability to retain its icosahedral structure on such supports, whereas on alumina the metal-support interaction is sufficient to stabilise the normally favoured crystal form of the cubooctahedron. The results of Del Angel *et al.*[53] with rhodium catalysts do indeed suggest that weak interactions with the support may significantly alter the catalytic properties of the

metal[53].

Due to its higher activity the 2-methylbutane reaction over Rh/Nb_2O_5 was studied at lower temperatures than those used for Pt/Nb_2O_5. At these temperatures single bond rupture was predominant with very little isomerisation observed, but as already mentioned, the n-pentane formed, although only reacting twice as fast when studied as a single reactant, competed successfully for the catalyst surface.

Comparison of the initial product distributions from 2-methylbutane and n-pentane hydrogenolysis over the supported rhodium catalysts, table 4.4, indicates that there was reasonably good agreement. The only difference being that the silica-supported sample has a propensity for scission of the secondary-tertiary C-C bond in 2-methylbutane. In a comprehensive study of alkane hydrogenolysis over Rh/SiO_2[18] it was proposed that the reactivity of the different types of bonds in alkanes was in the order S-S>P-S>S-T>P-T>P-Q, where P, S, T and Q represent primary, secondary, tertiary and quaternary carbons respectively. Thus n-pentane, because it contains more S-S and P-S bonds than 2-methylbutane reacts more quickly. Using 2,2-dimethylbutane as a model reactant, where the main reaction involves scission of the P-S bond to yield methane and 2,2-dimethylpropane, it was concluded that the main mechanism of hydrogenolysis was 1,2-type with only minor contributions from 1,3-intermediates.

However, as indicated by Clarke *et al.*[54] a 1,4-adsorption forming a metallocyclopentane with further ring contraction may be an alternative to the 1,2-process. The main reaction observed with 2-methylbutane over Rh/Nb_2O_5 was the production of methane and 2-methylpropane, table 4.4, thus a 1,2- or a 1,4-process could be intimated.

The activation energy calculated for 2-methylbutane hydrogenolysis over Rh/Nb_2O_5 was rather less than that found for the same reaction over Rh/SiO_2[18], but it has been observed that for methylcyclopentane hydrogenolysis an increase of activation energy is generally expected as dispersion increases[53].

4.4.3 Kinetic Studies over HTR Catalysts

An important feature of SMSI is the ability of the activity of the LTR catalyst to be regenerated by an oxidation treatment. As tables 4.2, 4.3 and 4.4 show the activities of all three catalysts Pt/TiO_2, Pt/Nb_2O_5 and Rh/N_2O_5 after HTR were recovered and, except for the titania supported sample, the initial product distributions were fully duplicated, table 4.2. This discrepancy may be due to the reported difficulty of the reversal of Pt/TiO_2 catalysts in the SMSI state[32].

After HTR all three catalysts showed little activity for 2-methylbutane hydrogenolysis, suppression factors of 10, 600 and 10^5 being recorded for Pt/TiO_2, Pt/Nb_2O_5 and Rh/Nb_2O_5 respectively. The large factor found for Rh

is a consequence of the greater hydrogenolysis activity of that metal, and although all the catalysts are thought to have a poor dispersion the catalytic activity of both of the niobia-supported materials are suppressed more than the titania sample. Adsorption measurements on TiO_2 and Nb_2O_5 supported nickel have indicated that hydrogen chemisorption was always more severely suppressed with Nb_2O_5 as the support[55]. This was also reported to be the case for supported Ir catalysts[56]. It was concluded that the extent of interaction of the metal with the support correlated with the reducibility of the support, with Nb_2O_5 being more susceptible to reduction than TiO_2. In spite of the fact that activities for 2-methylbutane hydrogenolysis over HTR Pt/TiO_2 were variable the initial product distributions indicated that deeper hydrogenolysis was occurring, and although the n-pentane formed was of a similar amount as over the LTR catalyst it did not compete as successfully for the surface. This was more pronounced with the HTR Pt/Nb_2O_5 sample over which the reaction of 2-methylbutane self-poisons and, as shown by figure 4.7, the amount of n-pentane decreased linearly with time. This would seem to suggest that the nature of the active sites, as well as their concentration, was affected by HTR.

The large amounts of isomerised product formed over HTR Pt/Nb_2O_5 and Rh/Nb_2O_5 from both n-pentane and 2-methylbutane suggests that by suppressing the amount of

adsorbed hydrogen and hence hydrogenolysis, the isomerisation process (perhaps via a metallocyclobutane intermediate as previously proposed) is significant over these catalysts. The appearance of alkene in the gas phase over Pt/Nb_2O_5 may also be a consequence of the lower concentration of adsorbed hydrogen. Although under the reaction conditions used some alkene should be present on thermodynamic arguments none is observed over the Pt/TiO_2 and Rh/Nb_2O_5 catalysts, thus the presence of alkene appears to be specific to the Pt/Nb_2O_5 system. Dehydrogenation of butane over HTR Ir/TiO_2 has also been reported[37]. As the dehydrogenation product appeared after a lower catalyst reduction temperature than the isomerised product, it has been suggested[37] that the dehydrogenation proceeded through a different reaction path unrelated to the intermediate in the C_3-cyclic mode hydrogenolysis and isomerisation.

4.4.4 Exchange Studies

The similarity of the results from exchange of 2-methylbutane over Pt/Nb_2O_5 and Pt/SiO_2 shows that under LTR conditions the niobia remains for this reaction essentially a non-interacting support, and at 355K the exchange reaction is $5x10^5$ times more efficient than the hydrogenolysis reaction. Formation of moderate amounts of the d_1-product by stepwise exchange is typical of hydrocarbon exchange over platinum as is the small maximum

observed for the perdeuteromolecule[11,57]. Previous exchange studies with cyclopentane over LTR and HTR Rh/TiO_2 had suggested that this reaction may be structure sensitive[41], with the rate of reaction being suppressed by a factor of 500 and the initial product distributions being different from that expected as a consequence of temperature effects only. In the present study the exchange activity of the Pt/Nb_2O_5 sample was suppressed by a factor of 10^4, a much larger degree than that observed for 2-methylbutane hydrogenolysis. The observed changes in the initial product distributions between LTR and HTR Pt/Nb_2O_5, however, can only be attributed to the change in reaction temperature, although a greater variation than that observed may have been expected considering the large difference in temperatures used.

The formation of alkene at the higher reaction temperatures required to study HTR catalysts did not affect the production of exchanged products as indicated in figure 4.10, which would be compatible with the existence of two different types of active site. One is probably platinum metal unaffected by the migration of the oxide support which effects the exchange reaction and the other is where alkene is produced, probably at the metal/metal oxide interfaces induced by HTR.

W EVIDENCE ON THE MECHANISMS OF EXCHANGE REACTIONS OF ALKANES ON METALS FROM THE ANALYSIS OF PRODUCTS BY DEUTERIUM NMR SPECTROSCOPY

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ABSTRACT

The exchange of a number of hydrocarbons with deuterium over supported dium, palladium, platinum and rhodium catalysts has been followed by mass ectrometry and the products analysed by deuterium NMR spectroscopy. The oupings of deuterium atoms in the products gave evidence about adsorbed termediates and probable mechanisms for the reactions. Results confirmed e accepted view that interconversion of adsorbed alkyl and alkene was an portant process on palladium and platinum. Reactions on rhodium also volved 1,3- and 1,4- adsorbed intermediates. Iridium gave preferential change of primary C-H bonds and showed little tendency to promote multiple change with most hydrocarbons.

INTRODUCTION

The study (1-3) of exchange reactions of alkanes with deuterium has elded much evidence about the nature and reactivity of adsorbed termediates and so supplied information which is fundamental to an derstanding of the mechanisms of hydrocarbon reactions on metals. Many drocarbon/metal systems show evidence of substantial amounts of multiple change, the replacement of many or all of the hydrogen atoms in a single sit of the molecule to the catalyst surface. Such reactions may occur rough the ready interconversion of adsorbed alkyl and alkene species (the -called $\alpha\beta$-process) or by interconversion of alkene and allyl species (the γ-process). Recently, (4,5) the use of high field deuterium NMR ectroscopy has provided a means of identifying the groupings of deuterium oms in the products of exchange reactions and of estimating antitatively the distribution of the atoms in the various groupings. sults obtained in this way are more revealing than those from the ditional mass spectrometric technique and have necessitated a revision of ne of the accepted ideas about the mechanisms of exchange reactions.

The present research which is a continuation of the previous work (5) amined the behaviour of the model compounds propane, n-butane, methylpropane, 2-methylbutane and 2,2-dimethylpropane over the metals idium, palladium, platinum and rhodium, used as supported catalysts. 2,3,3-Tetramethylbutane was also reacted over rhodium.

EXPERIMENTAL

The hydrocarbons and the deuterium (99.5%) were purchased from Cambrian emicals Ltd. The preparation and pretreatment of the platinum and rhodium talysts, each with 10^{-4} mol metal/g silica, have been described (6). Two dustrial supported palladium catalysts with markedly different ncentrations of metal were pretreated in the same way (6); Pd(A), from hnson Matthey, contained 4.7×10^{-4} mol metal/g charcoal and Pd(B), from

CI, had 2.5 x 10^{-6} mol metal/g calcium aluminate. The iridium catalyst ontained 2 x 10^{-5} mol metal/g γ-alumina (7)

Reactions were carried out in a static system linked to a VG Micromass M-601 mass spectrometer (8). Most experiments were run with a 5:1 mixture f deuterium:hydrocarbon and a charge of about 2 x 10^{20} molecules of ydrocarbon in the reactor (240 cm^3). Conditions were chosen to give about 5% exchange in about 1h. Then the hydrocarbon was condensed in a trap held n liquid nitrogen, transferred to an NMR-tube containing 5% $CDCl_3$ in $CHCl_3$ nd analysed using a Bruker WH 360 spectrometer at 55.28 MHz as previously escribed (5).

RESULTS AND DISCUSSION

Mass spectrometric analyses of samples of n-butane subsequently xamined by NMR are given in table 1. For each of the metals, the product istributions with propane, 2-methylpropane and 2-methylbutane were broadly imilar to those shown for n-butane. The monodeuteroproduct was always rominent with iridium and there was little multiple exchange. Platinum ended to give U-shaped distributions with appreciable amounts of the onodeuteroproduct as well as significant and extensive multiple exchange.

ABLE 1. Product distributions for exchanged butanes

atalyst	Ir	Pd(B)	Pt	Rh
emperature (K)	334	452	332	332
ime (min)	78	22	94	79
eight (mg)	76	513	52	9
umber of D atoms		Percentages of products		
0	79.35	84.24	91.25	92.60
1	17.60	1.02	3.09	0.85
2	2.55	0.16	0.96	0.55
3	0.29	0.14	0.70	0.40
4	0.07	0.07	0.65	0.38
5	0.04	0.32	0.60	0.36
6	0.04	0.52	0.49	0.33
7	0.02	1.27	0.45	0.43
8	0.01	2.56	0.39	0.61
9	0.01	4.72	0.50	1.20
10	0.02	4.98	0.92	2.29
ean number of D er exchanged molecule	1.20	8.15	4.07	6.76

he dominant reaction with rhodium and palladium was very extensive multiple xchange with the perdeuteroproduct appearing as a major product at low onversions.

The simplest information gained from the NMR analyses of the exchanged roducts was the relative amounts of deuterium present in the primary, econdary and tertiary positions in the hydrocarbons, table 2. Iridium was nique in exhibiting a high preferential exchange of primary hydrogen atoms. his suggests that some kind of heterolytic dissociation may by occurring on ridium leading to the formation of partially charged R^- and H^+ species ssociated with the surface atoms. Both types of palladium catalyst showed imilar behaviour and tended to exchange all hydrogen atoms to similar xtents. Platinum gave some preferential exchange of secondary and tertiary ydrogen atoms although the monodeuteroproducts from the reaction of propane nd butane showed the same extent of exchange in primary and secondary osítions. These results contrast with those reported by Lebrilla and Maier 9) who obtained evidence that the monodeuterohexane formed under the onditions they used with platinum contained mainly primary deuterium.

TABLE 2. Relative extents of exchange per primary, secondary or tertiary hydrogen atom in the hydrocarbons

Catalyst		Ir	Pd(A)	Pd(B)	Pt	Rh
Typical temperature (K)		334	426	440	333	319
Propane	($2^0/1^0$)	<0.01	1.00	1.00	1.10	0.75
Butane	($2^0/1^0$)	0.05	-	1.05	1.55	1.10
2-Methylpropane	($3^0/1^0$)	≈0.1	1.05	1.00	1.50	0.90
2-Methylbutane	($2^0/1^0$)	<0.01	-	1.10	1.40	1.10
2-Methylbutane	($3^0/1^0$)	<0.01	-	1.10	1.55	1.15

Rhodium behaved like palladium but showed a lower tendency to exchange secondary hydrogen in propane or tertiary hydrogen in 2-methylpropane.

Groupings of deuterium atoms detected by NMR. The results in figure 1 for 2,2-dimethylpropane show how it was possible to use the NMR analyses to identify and estimate groupings of deuterium atoms in the exchanged products because of the existence of isotopic shifts due to neighbouring deuterium atoms. Earlier work (5) indicated that the isotopic α, β and γ shifts

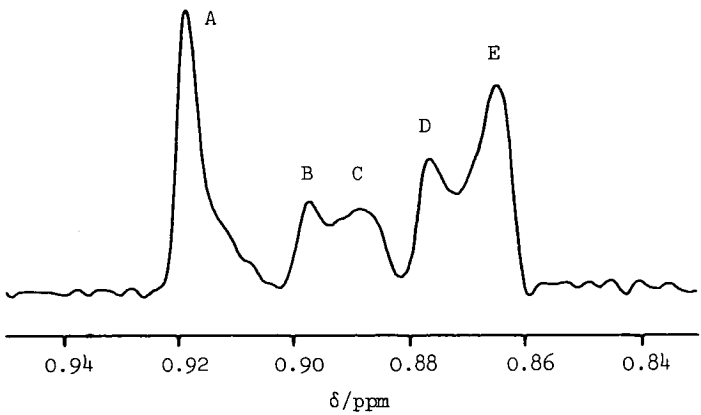


FIGURE 1. Line-narrowed NMR spectrum of 2,2-dimethylpropane from the exchange of an 8:1 deuterium:hydrocarbon mixture over 5mg of Rh/SiO_2 at 450K for 30 min. The resonances are:- A, $-CH_2D$; C and B, $-CHD_2$ with and without γ shifts; E and D, $-CD_3$ with and without γ shifts.

caused by deuterium atoms separated by two, three or four bonds respectively from the observed deuteron were about -20, -8 and -1 p.p.b. The resonances due to $-CH_2D$, $-CHD_2$(1α shift) and $-CD_3$(2α shifts) are easily distinguished as peaks A, B and D in figure 1. The remaining resonances C and E correspond to $-CHD_2$ and $-CD_3$ in molecules substantially exchanged in the other three methyl groups resulting in a detectable separate resonance through the combined influence of several γ shifts. It was always possible to identify an α shift, generally possible to detect a β shift but only feasible to see γ shifts when more than five or six were involved. The groupings of relevance to understanding mechanisms will be presented and discussed for each of the reactants.

ropane The amounts of primary deuterium in some of the important groupings re given in table 3. Calculated distributions were based on the assumption hat multiple exchange involved the αβ-process and derived from product istributions determined by the mass spectrometer. Thus, the D_2-compound as assumed to be $CH_2DCHDCH_3$ and the D_3-compound was assigned to CHD_2CHDCH_3, $H_2DCD_2CH_3$ and $CH_2DCHDCH_2D$ in proportions of 2:1:3 respectively. Further xchange was assumed to involve random replacement of the remaining ydrogen atoms. There was good agreement between the calculated and

ABLE 3. Some groupings of primary deuterium atoms in exchanged propanes

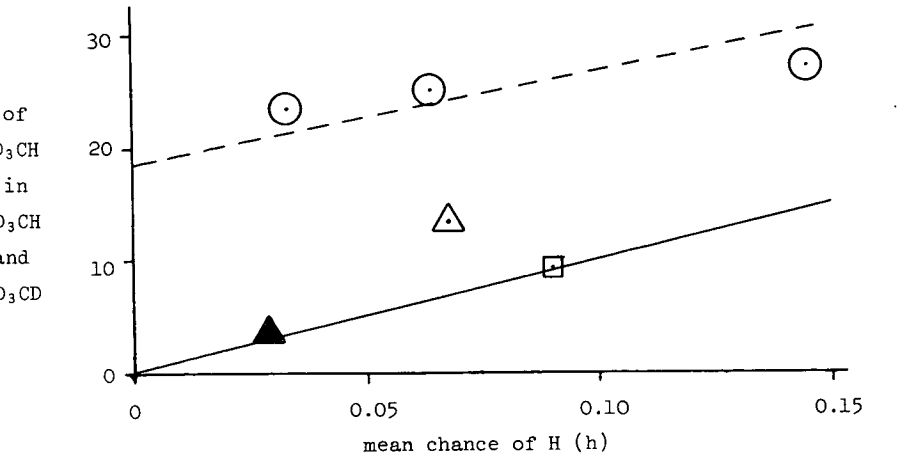
	Percentages of total primary deuterium						
atalyst	Pd(A)		Pt		Rh		Ir
exchange	22.4		10.6		8.5		17.7
emperature (K)	426		353		331		335
rouping	obs.	(calc.)[a]	obs.	(calc.)[a]	obs.	(calc.)[a]	obs.
H_2DCH_2-	3.7	(2.6)	10.8	(9.0)	4.7	(2.1)	88.4
H_2DCHD -	3.1	(2.7)	7.6	(7.1)	1.5	(6.1)	0
H_2DCD_2-	} 2.2	(2.0)	} 3.4	(3.1)	} 7.4	(3.9)	0
HD_2CH_2		(0)		(0)		(0)	11.6
D_3CHD-	}71.2	(9.2)	}57.7	(7.7)	41.4	(11.6)	0
D_3CD_2-		(63.2)		(51.7)	24.4	(46.6)	0

[a]Calculated for an αβ-process, see text.

bserved distributions for palladium and platinum confirming that an αβ-process can account for the multiple exchange with these metals. The ituation with rhodium was different; observed results gave too little CH_2DCHD- and CD_3CD_2- and too much of the other groupings in relation to the alculated values. These results can be understood if it is assumed that ome multiple exchange occurs by an αγ-process, i.e. interconversion between dsorbed n-propyl radicals and 1,3-diadsorbed species.

2-Methylpropane The main grouping of interest was CD_3CH -. If the echanism of multiple exchange involves either an αβ- or an αβγ-process this grouping should not be formed in the initial reaction because both echanisms will replace the tertiary hydrogen atom. Subsequently, the mount of CD_3CH should rise as the deuterium becomes diluted with HD and the ean chance (h) of acquiring H (instead of D) increases. Calculations of h rom the initial and final compositions of the reacting gases is simple. he results in figure 2 for platinum and palladium lie close to the line xpected for an αβ-process, those for rhodium are well above. So once again he multiple exchange on rhodium must involve a contribution, of about 20%, rom an αγ-process, or possibly an αα-process giving multiple exchange of a ethyl group through the formation of adsorbed carbene species (1).

2,2-Dimethylpropane Previous work (10, 11) has established that there are hree mechanisms of exchange of this molecule:- stepwise exchange (I), ultiple exchange limited to one methyl group (II) and multiple exchange anging over the whole molecule (III). Rhodium, having the ability to perate an αγ-process, is known to be one of the most effective catalysts or (III). The results in figure 1 show that NMR analysis can provide uantitative data about the contribution of the mechanisms to the overall exchange; peak A represents products from I, peaks B and D products from II, nd peaks C and E molecules resulting from mechanism III. Results in



of
D_3CH
in
D_3CH
and
D_3CD

GURE 2. Percentage of CD_3CH - related to the mean chance of acquiring an atom during the reaction; ⊡Pt(365K), ▲ Pd(A) (426K), ▲ Pd(B) (426K), Rh (296, 319 and 332 K); full line - results expected for an αβ-process, shed line - expected for a 19% contribution from an αγ- (or αα-) process.

ble 4 show the influence of deuterium pressure on the overall rate of change and the contributions of the individual mechanisms determined by R analysis. The overall rate was inhibited by deuterium presumably cause it was more strongly adsorbed than the hydrocarbon. The additional

BLE 4. Influence of deuterium pressure on the exchange of 2,2-dimethyl-opane (4.4 kPa) on rhodium at 450K

uterium essure (kPa)	Total rate $r/10^{22}$ molecule s^{-1} $(mol\ Rh)^{-1}$	Percentage contribution of mechanisms		
		I	II	III
8.8	9.8	30	12	58
17.5	5.3	38	12	50
35	4.1	46	17	37
essure dependence	-0.5	-0.3	-0.3	-1.0

gative dependence for III may arise through the mechanism involving a more ssociated form of the hydrocarbon or possible an additional surface site.

Results for the exchange of 2,2-dimethylpropane on all four metals are mpared in table 5. There are marked differences in the extent of multiple change with this compound which is unable to dissociate to an adsorbed kene and the results with the other reactants, already described. The eaction with palladium was almost entirely stepwise since the amount of CHD_2, corresponded mainly to products which had undergone successive change. This means that palladium which is the most effective metal for ltiple exchange by the αβ- and αβγ- processes is unable to catalyse the - and αγ- mechanisms required for II and III. The converse occurs with idium. Although it gave only stepwise exchange with the other drocarbons, significant contributions from mechanisms II and III are found th 2,2-dimethylpropane. Platinum shows some multiple exchange but differs om rhodium and iridium in not giving a separate peak for $-CD_3$ with γ ifts. The extent of the exchange by mechanism III is obviously less with

platinum than with the other two metals.

TABLE 5. Distributions of deuterium in exchanged 2,2-dimethylpropane using a 4:1 mixture on Rh and 5:1 on the other metals.

Catalyst	Pd(B)	Pt	Ir	Rh
Temperature (K)	460	431	450	450
Percent exchange	20.3	14.4	16.7	14.1
Grouping	Percentage of total deuterium			
$-CH_2D$	93	63	73	28
$-CHD_2$ without γ shifts	7	} 25	} 13	7
$-CHD_2$ with γ shifts	0			22
$-CD_3$ without γ shifts	0	} 12	8	9
$-CD_3$ with γ shifts	0		6	34

2,2,3,3-Tetramethylbutane With this molecule an $\alpha\gamma$-process can lead to multiple exchange but limited to the three methyl groups attached to each of the central carbon atoms. Recent work (12) has shown that more extensive exchange involving all six methyl groups occurs with rhodium and provided evidence for multiple exchange by $\alpha\delta$-intermediates. NMR analysis of a sample 13.7% exchanged over rhodium at 393K confirmed the previous conclusions. Some 31% of the deuterium was present in the groupings $-CH_2D$ and $-CHD_2$ resulting from mechanisms I and II described for 2,2-dimethylpropane but 58% appeared in a resonance with a total isotopic shift of -55 p.p.b. corresponding to $-CD_3$ in highly exchanged molecules. The alpha shifts accounted for -40 p.p.b. of this total shift and the remaining -15 p.p.b. represented the combined effect of up to six gamma and nine delta shifts.

CONCLUSIONS

NMR analysis of the early products from hydrocarbon exchange reactions is a powerful technique for obtaining data useful for defining possible mechanisms. Our evidence shows that the $\alpha\beta$-process is adequate to explain the results for the multiple exchange of propane on palladium or platinum. It is not necessary to invoke an $\alpha\beta\gamma$-process as well although the possibility that it makes some contribution cannot be excluded. Lebrilla and Maier (9) suggested that the main mechanisms over platinum are stepwise exchange (for primary hydrogen) and an $\alpha\beta\gamma$-process for multiple exchange with little role for an $\alpha\beta$-process. Their combination of mechanisms provides a possible explanation of the significant proportion of monodeuteroproducts for the reactions of hydrocarbons on platinum. But it is relevant to note that the D_1 compound is also a major product for the exchange of ethane on platinum (5). The production of a singly-exchanged species seems to be a general feature of the behaviour of platinum rather than a consequence of the relative rates of the $\alpha\beta$- and $\alpha\beta\gamma$-processes.

The relative importance of the various mechanisms and the role and reactivity of the hydrocarbon intermediates may be influenced by a number of factors such as the crystal faces exposed, dispersion, interactions with the support and the source of the labelling deuterium. The effect of some of these factors was shown by Long et al. (13) who obtained results using proton NMR on the relative exchange of primary, secondary and tertiary hydrogens for various hydrocarbon/metal film systems. But perhaps the most striking feature is the relatively small variation in behaviour of any given metal in exchange reactions with the form in which it is used (1-3). For a range of hydrocarbons each metal tends to give product distributions characteristic of itself and only influenced to a lesser degree by the other factors listed above. The differences between the metals are obvious and easy to discern if a range of reactants are used. It is unlikely that geometrical considerations can account for the large variations in

haviour of the four metals under discussion. All form f.c.c. crystals d the metal-metal spacings range only from 269 pm (Rh) to 275 pm (Pd). e main conclusions about the catalytic behaviour for the hydrocarbon actions can be summarised briefly.

idium The main characteristic of this metal is the preferential exchange primary hydrogen atoms in the hydrocarbons. There is little tendency for ltiple exchange to occur except at higher temperatures with molecules such 2,2-dimethylpropane which can form αα- and αγ-intermediates by ssociation of primary C-H bonds.

lladium This metal is the most effective for multiple exchange of any drocarbon for which an αβ-process is possible. Even at higher mperatures it is the poorest catalyst for forming αα- or αγ-intermediates. e 100-fold change in loading had little influence on the character of the actions.

odium The ability to form αγ- and αδ-intermediates in addition to erating the αβ-process is the main characteristic of this metal. In some ys it is the most versatile of the four metals and involves the greatest riety of intermediates and mechanisms, even with simple molecules.

atinum This metal apart from a tendency to promote some stepwise change has properties which resemble rhodium with 2,2-dimethylpropane and lladium with the less branched molecules.

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Mechanistic studies of the reactions of 2-methylpropene with deuterium over supported metal catalysts

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Deuterium NMR spectroscopy, gas chromatography and mass spectrometry have been used to examine the products from the reaction of 2-methylpropene with deuterium over supported metal catalysts. The detailed information, so obtained, about the number, location and grouping of deuterium atoms in both the exchanged alkenes and the 2-methylpropanes formed by addition provided evidence about possible mechanisms.

With palladium, exchange was faster than addition and the deuterium atoms were randomly distributed in the alkene, probably through a π-allyl dissociative mechanism. With platinum and rhodium, exchange occurred preferentially in the methylene groups of the alkene and the results indicated a dissociative mechanism involving adsorbed vinyl intermediates together with some intramolecular double-bond movement through a π-allyl type of species. Relatively little exchange occurred with iridium.

The activities of the metals for production of alkane at 235 K were Rh > Ir > Pd > Pt but the spread was only a factor of about 20. With all metals except palladium further exchange occurred during the addition process, but this was mainly concentrated in one methyl group. This behaviour was explained in terms of mechanisms that permitted additional exchange of the methylene group of the alkene to take place during the addition process.

Introduction

Deuterium has been used extensively to attempt to establish the mechanisms of the various reactions of alkenes on metal catalysts. An important component of these mechanisms has been the reversible formation of adsorbed alkyl radicals on the catalyst surface, the so-called 'half-hydrogenated state' as defined by Horiuti & Polanyi (1934). Reactions such as exchange of the alkene with deuterium and the isomerization of alkenes can be explained satisfactorily in many cases by these alkyl reversal processes that are classified as associative mechanisms (Bond & Wells 1964). Some success has been achieved in a quantitative interpretation of the amounts of the various isotopic ethenes and ethanes formed from the reaction of C_2H_4 and D_2 on evaporated metal films (Kemball 1956) in terms of the relative rates of the various reactions of adsorbed ethene and adsorbed ethyl species and the same approach has been extended to results over alumina-supported platinum

and iridium catalysts (Bond *et al.* 1964). The possibility that exchange of ethene might occur through some kind of dissociative mechanism was suggested at an early stage (Farkas *et al.* 1934) and a role for such mechanisms has been proposed for the exchange and isomerization of larger alkenes, e.g. for reactions of but-1-ene with perdeuteropropene on palladium films (Ledoux *et al.* 1978).

Many investigations with propene as reactant have been carried out to establish the relative contributions of associative and dissociative mechanisms on metals and considerable use has been made of microwave spectroscopy as a means of locating the positions of the deuterium atoms in the exchanged propenes. Some of the pioneering work by the Japanese has been reviewed by Hirota (1973) and recent studies have included reactions of propene over supported palladium (Naito & Tanimoto 1986) and over supported nickel and platinum (Naito & Tanimoto 1987). There is now clear evidence that dissociative mechanisms involving vinyl species (both propen-1-yl and propen-2-yl) do contribute to the exchange of propene but to an extent which varies with the metal. However, the latest results obtained by Naito & Tanimoto (1987) suggest that associative mechanisms prevail in the presence of gas phase deuterium and that the dissociative processes are largely suppressed. In some ways, propene with three distinguishable types of vinyl hydrogen is too complex a molecule for mechanistic studies and it seemed to us that an investigation into the relative contributions of associative and dissociative processes could be made more satisfactorily by using 2-methylpropene because the molecule has only a single pair of identical vinyl hydrogen atoms.

There is comparatively little work on the reactions of 2-methylpropene with deuterium on metal catalysts in contrast to the numerous studies with ethene or propene. An early investigation on a nickel catalyst (Wilson *et al.* 1953) showed that the main product was D_2-alkane in contrast to the spread of isotopic products obtained with other alkenes. Hirota *et al.* (1977) used microwave spectroscopy to analyse the alkenes and alkanes obtained from 2-methylpropene reactions on various supported metal catalysts and related organometallic complexes. They concluded that the main mechanisms of exchange were alkyl reversal with some contributions from π-allyl species but they found no evidence of a role for vinyl species. Microwave spectroscopy, although it is a sensitive technique capable of examining small samples, is not ideally suited for determining the position of deuterium atoms in 2-methylpropene because of the complexity of the rotational spectra, and it is even less satisfactory with 2-methylpropane which has a lower dipole moment. Deuterium NMR spectroscopy, on the other hand, provides a very useful technique for obtaining detailed information on the distribution and grouping of deuterium atoms in the products from the reactions of 2-methylpropene and deuterium as shown by recent work with various oxide catalysts (Bird *et al.* 1986).

The objective of the present work was to use the technique of deuterium NMR spectroscopy combined with mass spectrometry and gas chromatography to examine the products from the reaction of 2-methylpropene with deuterium on a range of supported metal catalysts. The emphasis of the work was directed towards the determination in some detail of the distributions of deuterium atoms in the products and not on the evaluation of rates or other kinetic parameters. We

hoped that such information might provide a clear indication of the relative roles of associative and dissociative mechanisms for the reactions of 2-methylpropene on the metals and the contributions of vinyl or allyl species in the dissociative processes.

Experimental

Materials

Deuterium and 2-methylpropene, both 99.5% purity, were obtained from Matheson Gas Products. Deuterium was further purified by diffusion through a palladium–silver thimble and the alkene was subjected to several freeze–pump–thaw cycles before use. Helium, BOC grade, was purified by passing it through an oxygen trap, Alltech Ltd, and a molecular sieve held at liquid nitrogen temperature.

The preparation and pretreatment of the rhodium catalyst (10^{-4} mol Rh g^{-1} silica, dispersion 0.92) have been described (Wong *et al.* 1984) and similar details are available (Faro *et al.* 1983) for the iridium catalyst (2.5×10^{-5} mol Ir g^{-1} γ-alumina, dispersion 0.78). The palladium catalyst was supplied by ICI; it had a low loading of 2.5×10^{-6} mol Pd g^{-1} calcium aluminate and was pretreated in the same way as the rhodium catalyst. The platinum catalyst was prepared by impregnation of niobia, batch CBMM AD 317, supplied by the Brazilian Company of Metallurgy and Minerals and similar to material described by Iizuka *et al.* (1983). Before impregnation, the niobia was washed several times with distilled water, dried overnight at 383 K and calcined for 16 h at 773 K, the highest temperature to which the catalyst would subsequently be heated. After calcination the surface area, measured by the BET method, was 50 m^2 g^{-1}. Chloroplatinic acid (Johnson Matthey) was used for the impregnation and after drying at room temperature for 24 h, the catalyst was calcined overnight at 383 K. Further treatment to stabilize the catalyst before storage involved reduction at 773 K in flowing hydrogen (2 h), oxidation at 673 K (1 h) and cooling to room temperature in flowing oxygen. The loading of platinum was 5.1×10^{-5} mol Pt g^{-1} niobia and dispersion about 0.30. Before use the catalyst was subjected to one of two treatments: low-temperature reduction (LTR) was carried out with flowing hydrogen at 523 K for 2 h and evacuation for 30 min before cooling to reaction temperature or high-temperature reduction (HTR) involving a similar procedure but at 773 K.

Apparatus

The experiments were carried out in an all-glass recirculating system similar to that described by Bird *et al.* (1986) but fitted with a continuous leak to a Vacuum Generators Micromass 601 mass spectrometer as well as a gas sampling valve to enable samples to be analysed by gas chromatography. There was a by-pass to the section containing the catalyst so that it was possible to expose the reactants to the catalyst for limited periods without interrupting the circulation. The total volume of the recirculation system was 360 cm^3. The pressure of alkene was 2.7 kPa, corresponding to a charge of 2.3×10^{20} molecules and the normal ratio of deuterium to hydrocarbon was 5:1. Some experiments were carried out with a 1:1 mixture and the balance was made up with helium. The extent of conversion

to alkane was determined by the gas chromatograph that was a Perkin–Elmer F33 fitted with a flame ionization detector. Separation of the gases was achieved using a column (2 m) containing 3% (by mass) squalane on activated alumina at 378 K with a pressure of 241 kPa of nitrogen carrier gas.

Samples for analysis by NMR spectroscopy were obtained by condensing the hydrocarbons in a liquid nitrogen trap after about 15 to 20% of alkane had been formed and subsequently distilling them into an NMR sample tube containing chloroform with 5% D. Details of the procedure have been described by Brown *et al.* (1986) and Bird *et al.* (1986). Mass spectrometric analyses were also made on the reaction mixture after the required amount of addition had occurred and the catalyst had been isolated. These were obtained by using 15 eV electrons to ionize the molecules. At this voltage, calibration experiments showed that the sensitivity for the alkene parent ion ($m/e = 56$) was 18 times that for the alkane parent ion ($m/e = 58$). When the exchange of the alkene was not extensive, peaks from $m/e = 60$ upwards were assigned to isotopic alkanes and the usual correction made for naturally occurring isotopes and fragmentation. In this way the relative amounts of D_2- and more highly deuterated alkanes were determined. The residual peaks from $m/e = 56$ to $m/e = 59$ were used to estimate the relative amounts of the D_0- to D_3-alkenes. In some of the experiments which were carried out after the sensitivity of the ion multiplier in the collector of the mass spectrometer had been improved, it was possible to obtain kinetic analyses for the exchange of the alkene by using an ionizing voltage of 9 eV. With this voltage the contribution from the alkanes was negligible.

Results

NMR analyses

The NMR spectra corresponding to deuterium in 2-methylpropene were similar to those already reported (Bird *et al.* 1986). The groupings CHD= and CD_2= gave resonances at $\delta = 4.689$ and 4.674 p.p.m.† corresponding to an α-shift of −15 p.p.b.‡ caused by the presence of the second D atom. The resonance from $-CH_2D$ occurred at $\delta = 1.722$ p.p.m. and the corresponding α-shift for $-CHD_2$ was −19.5 p.p.b. Spectra for the alkanes were also similar to those given previously by Brown *et al.* (1985) and Bird *et al.* (1986). A spectrum including the region covering the tertiary deuterium atom is shown in figure 1. The large peak at $\delta = 1.682$ p.p.m. corresponds mainly to the molecule $(CH_3)_2(CH_2D)CD$ in which the tertiary D atom is subject to a β-shift of about −7 p.p.b. as a result of the D atom in one of the methyl groups. The smaller peak at $\delta = 1.689$ p.p.m. is due to tertiary D in $(CH_3)_3CD$. In the experiment shown in figure 1 the alkene is not extensively exchanged and so the contribution of a peak due to $-CD_3$ in the alkene which should occur at $\delta = 1.683$ p.p.m. is likely to be small and will only amount to a low percentage of the large resonance at this position. In contrast, the spectrum shown in figure 2 for a sample after reaction over palladium has a broad resonance at $\delta = 1.683$ which included contributions both from $-CD_3$ in the

† p.p.m., parts per million.
‡ p.p.b., parts per thousand million.

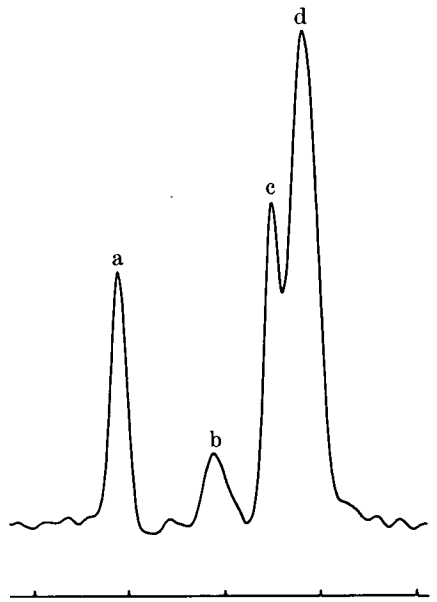


FIGURE 1. Part of the NMR spectrum from experiment Pt3 (LTR). The resonances a and b result from the methyl groups $—CH_2D$ and $—CHD_2$ of the alkene; the resonances c and d result from the tertiary D atom of 2-methylpropane as $CD(CH_3)_3$ and $CD(CH_2D)(CH_3)_2$ respectively.

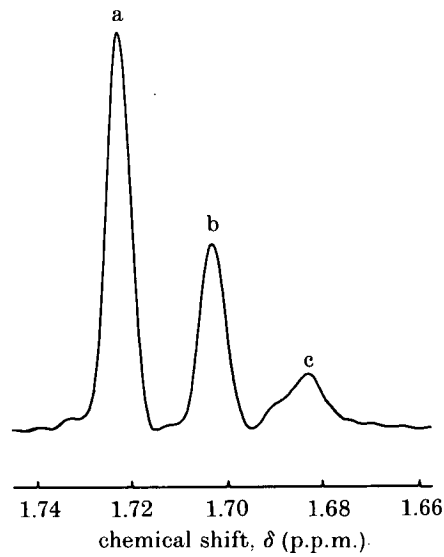


FIGURE 2. Part of the NMR spectrum from experiment Pd1 covering the same region as in figure 1. The resonances a and b result from the methyl groups $—CH_2D$ and $—CHD_2$ of the alkene. The small broad resonance c includes contributions from the $—CD_3$ group in the alkene and the tertiary D atom in the alkane.

alkene and tertiary D in the alkane and a direct estimation of the individual contributions was not possible. Figure 3 shows the sequence of resonances found for primary D atoms in the alkane in the products from two experiments. The peaks corresponding to $-CH_2D$, $-CHD_2$ and $-CD_3$ are well separated because the α-shifts are about −21 p.p.b. The two components of each of these peaks, depending on whether the tertiary atom was H or D, are obvious in every case, but sometimes only poorly resolved because the β-shift is about −8 p.p.b. Even where this resolution was incomplete, it was still possible to estimate what fraction of the molecules contained a D atom in the tertiary position from these spectra.

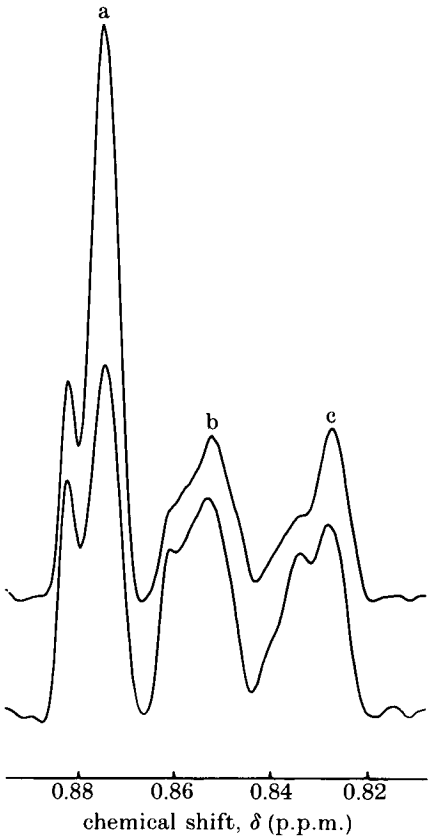


FIGURE 3. The NMR spectra for the primary D atoms in 2-methylpropane formed in the experiments Pt3 (LTR), upper curve, and Rh2, lower curve. Peak a corresponds to the groupings $CHCH_2D$ and $CDCH_2D$, b to $CHCHD_2$ and $CDCHD_2$ and c to $CHCD_3$ and $CDCD_3$.

The NMR analyses obtained for all the experiments together with information on weight of catalyst, time and temperature of the reaction, and percentage conversion to alkane are given in table 1. Experiments Rh1 and Rh2 were carried out by exposing the reaction mixture to the catalyst for a series of short periods.

TABLE 1. EXPERIMENTAL DETAILS AND NMR ANALYSES OF THE DISTRIBUTION OF DEUTERIUM IN THE HYDROCARBONS

		Pt1 (LTR)	Pt2 (LTR)[a]	Pt3 (LTR)	Pt4 (HTR)	Rh1	Rh2	Rh3	Ir1	Pd1
catalyst mass/mg		54	66	8.1	115	29	6.1	8.3	78	248
time/min		23	170	43	150	30	7	8	10	41
T/K		233	235	295	295	205	235	235	235	233
alkane (%)		13.9	17.0	18.3	20.8	18.2	20.9	99.6	23.1	19.2
D in alkene										
=CHD		5.4	5.1	4.2	7.9	2.9	2.2	—	—	15.1
$=CD_2$		—	1.0	1.4	1.3	1.0	0.8	—	—	3.8
$-CH_2D$		3.7	6.7	6.7	13.3	3.1	2.2	—	—	36.4
$-CHD_2$		—	1.2	2.7	2.6	—	0.8	—	—	17.9
$-CD_3$		—	—	—	—	—	—	—	—	9.0[c]
D in alkane										
3°D		39.2	37.5	29.5	25.6	29.4	27.2	24.1	47	9.0[c]
1°D[b]	$CHCH_2D$	—	(3)	5	(3)	6.2	6.3	(5.7)	—	6.5
	$CDCH_2D$	37.0	(32.6)	25.7	(23.3)	21.1	20	(18)	43	3.5
	$CHCHD_2$	—	6.9	(3)	(2.3)	17.6	(7.1)	(7.8)	—	3.0
	$CDCHD_2$	7.6		(10.1)	(10)		(14.6)	(18.2)	10	2.0
	$CHCD_3$	—	6.0	(3)	(2)	18.7	(7.5)	(9.9)	—	1.0
	$CDCD_3$	7.1		(8.7)	(8.7)		(11.3)	(16.3)	—	1.8
		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] Using a 1:1 ratio of D_2:hydrocarbon.
[b] Values in parentheses represent approximate contributions from $CHCX_3$ and $CDCX_3$ groups.
[c] The combined percentage of D in these groups was 9.0.

Mass spectrometric analyses

Representative analyses including results for each of the four metals at 233 or 235 K are shown in table 2. Reliable analyses were obtained for Pt1 and Ir1 because the exchange of the alkene was not extensive and no alkanes were formed

TABLE 2. MASS SPECTROMETRIC ANALYSES OF THE ISOTOPIC 2-METHYLPROPENES AND 2-METHYLPROPANES CORRESPONDING TO SAMPLES EXAMINED BY NMR

	m/e	56	57	58	59	60	61	62	63	64	65	66	67	68
experiment	D_i (alkene)	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8				
	D_i (alkane)			D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}
Pt1	alkene	83.4	2.2	0.6	—	—	—	—	—	—				
	alkane			—	—	11.4	1.3	0.5	0.7	—	—	—	—	—
Ir1	alkene	85.9	0.6	0.3	—	—	—	—	—	—				
	alkene (9 eV)	86.5	0.3	0.1	—	—	—	—	—	—				
	alkane			—	—	20.1	1.7	0.8	0.5	—	—	—	—	—
Rh2	alkene	76.3	1.8	0.7	0.3	—	—	—	—	—				
	alkene (9 eV)	77.1	1.3	0.4	0.2	0.2	—	—	—	—				
	alkane			—	—	9.1	5.1	2.0	1.1	1.5	0.2	0.2	1.0	0.7
Rh3	alkane			15.3	14.9	28.7	13.0	8.5	4.7	3.7	3.5	3.3	2.7	1.7
Pd1	alkene	22.8	27.5	18.1	8.2	2.7	1.0	0.3	0.2	—				
	alkane (approx. values)			—	—	(12)	(5)	(2)	(1)	(0.2)				

with less than two D atoms. The values for the alkenes in parentheses included for Ir1 and Rh2 are those obtained by using 9 eV electrons. With Rh2 the method of analysis was less satisfactory because some highly exchanged alkene was formed and the interpretation of the NMR data which will be presented later indicated that some D_0- and D_1-alkane must have been present. These factors meant that the simple treatment to attribute the peaks at $m/e = 58$ and 59 to alkene and the peak at $m/e = 60$ to alkane was not correct. No problem was encountered with Rh3 because the conversion to alkane was complete. The results with Pd1 were the least accurate because of the very extensive exchange of the alkene. There was no simple method of deciding what fraction of the peaks in the range from $m/e = 58$ to $m/e = 63$ was attributable to alkanes. An approximate analysis was made by calculating the fraction of the sum of these peaks attributable to alkane to give the total percentage of alkane equal to the value determined by gas chromatography and arbitrarily assuming that the same fraction applied to each individual peak. The results for the alkenes which are more reliable than those for the alkanes did show that a range of isotopic alkenes were formed.

Rates

Although the main emphasis of the work was on the detailed analyses of the products, some observations were also made on the course of the reactions with time. Figure 4 shows results for Rh1 and Rh2, experiments in which the gases were exposed to the catalyst for a series of short periods with analysis by gas chromatography at the end of each period. There was evidence for an initial rapid conversion at 205 K followed by a steady rate of reaction. The results at 235 K not surprisingly show more scatter for the periods of exposure to the catalyst were

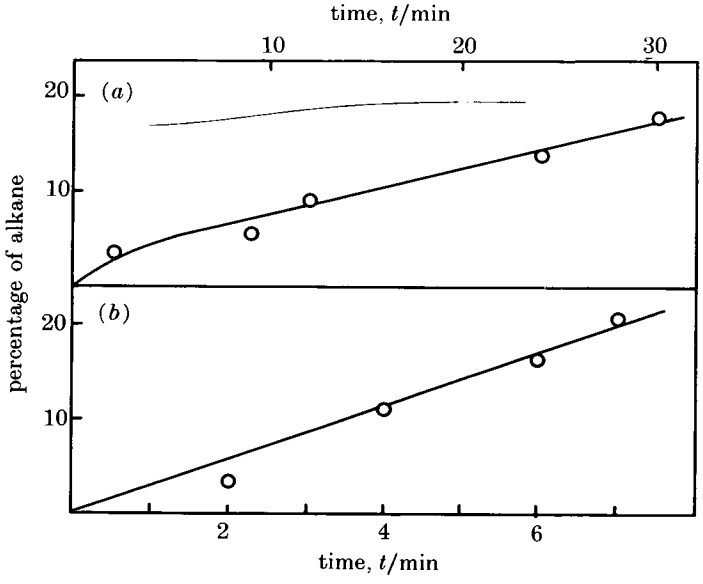


FIGURE 4. The course of the addition reaction with 2-methylpropene and deuterium over Rh/SiO_2 by using exposure of the gases to the catalyst for short periods; (*a*) at 205 K with 29 mg catalyst; (*b*) at 235 K with 6 mg catalyst.

short. Most of the experiments showed some evidence of an initial burst of activity, but rates could be determined from the subsequent part of the reaction which produced alkane at a steady rate or at a rate which decreased slightly with time.

More detailed results could be obtained in experiments in which the mass spectrometric analyses of the alkenes, by using 9 eV electrons, were made through the course of the reaction. The course of experiment Pt3 is shown in figure 5 which includes the increase in the percentage of total alkene exchanged as well as the increase of D in the alkene. The latter was measured by $\Phi = \sum_i iD_i$ where D_i is the percentage of the total alkene containing i deuterium atoms. The ratio of the gradients of these two curves associated with exchange gave a value of M, the mean number of D atoms acquired by each molecule undergoing exchange (Kemball 1959). Where kinetic data were not available, an approximate value of M was obtained from the average number of deuterium atoms in the exchanged

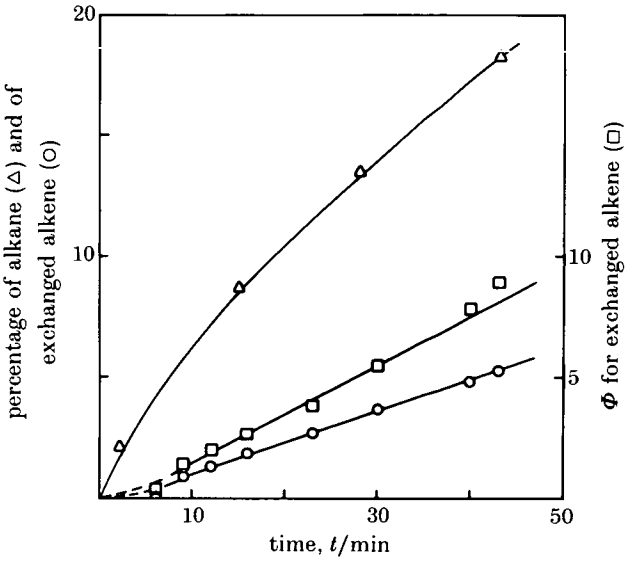


FIGURE 5. Course of the reaction of 2-methylpropene with deuterium in experiment Pt3 (LTR).

TABLE 3. RATES OF FORMATION OF ALKANE

experiment	T/K	D_2/alkene	
Pt1 (LTR)	233	5	13[a]
Pt2 (LTR)	235	1	1.7
Pt3 (LTR)	295	5	63
Pt4 (HTR)	295	4	4.7
Rh1	205	5	130
Rh2	235	5	300
Ir1	235	5	100
Pd1	233	5	53

[a] Units for this column are $10^3 r$ per molecule per second per metal atom.

alkene molecules, M_x, obtained from the mass spectrometric analyses such as those given in table 2. Rates of the formation of alkane, expressed in terms of the total amount of metal present and ignoring dispersion, are given in table 3. Values of M or M_x are included in table 4.

TABLE 4. INTERPRETATION OF THE NMR AND MS ANALYSES, AND THE DISTRIBUTION OF DEUTERIUM IN THE ALKENES

(Values in parentheses are subject to greater error.)

experiment	Pt1 (LTR)	Pt2 (LTR)	Pt3 (LTR)	Pt4 (HTR)	Rh1	Rh2	Rh3	Ir1	Pd1
tertiary D/alkane	1.00	0.90	0.80	0.85	0.77	0.70	0.69	1.00	0.35
primary D/alkane	1.32	1.16	1.51	1.64	1.67	1.72	2.17	1.13	1.52
total D/alkane (NMR)	2.32	2.06	2.31	2.49	2.44	2.42	2.86	2.13	1.87
total D/alkane (MS)	2.32	(2.40)	(3.15)	(3.49)	(3.04)	(3.64)	2.83	2.20	(2.68)
total D/alkene (NMR) (f)	0.037	0.072	0.091	0.22	0.051	0.041	—	—	1.60
total D/alkene (MS)	0.039	0.066	0.094	0.22	0.055	0.040	—	0.006	(1.33)
distribution in alkenes									
preferential exchange CX_2/CX_3	4.4	2.3	1.8	1.7	3.8	3.0	—	—	1.0
D/CX_2 group	1.00	1.09	1.14	1.08	1.15	1.15	—	—	1.11
D/CX_3 group	1.00	1.08	1.17	1.09	(1.0)	1.15	—	—	1.26
M or M_x	1.2	1.3	1.8	1.5	1.4	1.6	—	(1.2)	—
groups exchanged per molecule	1.2	1.2	1.5	1.4	(1.3)	1.4	—	—	—

INTERPRETATION OF RESULTS

The NMR results in table 1 provide information on the relative amounts of deuterium present in the various groupings in the alkenes and in the tertiary and primary positions in the alkanes in the samples analysed at the end of each experiment. These numbers were converted to absolute values by examining the detailed NMR spectra for the primary deuterium atoms in the alkane. In each experiment, it was possible to estimate the average fraction of tertiary D per alkane molecule by estimating the relative amounts of the groupings CH_2DCD and CH_2DCH, CHD_2CD and CHD_2CH, and CD_3CD and CD_3CH. Results derived in this way are shown in table 4. A different procedure was necessary for the results over palladium because of the overlap between the NMR resonances for $-CD_3$ in the alkene and for the tertiary D in the alkane. It was found that the distribution of deuterium in the various groupings in the alkene was close to a random distribution, as shown in table 5, with a chance $d = 0.20$ of a D atom in each position, i.e. 1.60 D atom/alkene in total. A simple calculation based on this value indicated that the 9.0% of deuterium in the combined peak had to be divided into 4.9% for $-CD_3$ in the alkene and 4.1% for tertiary D in the alkane in order to obtain tertiary D/alkane = 0.35 in agreement with the value estimated from the NMR peaks for the primary deuterium in the alkane.

The values of total D/alkene based on the NMR analysis were in good agreement with the mass spectrometer (MS) results in all cases except for Ir1 where the signals for deuterium in the alkene were too weak to be estimated and for Pd1 where the

TABLE 5. DISTRIBUTION OF DEUTERIUM IN THE ALKENE AFTER REACTION IN EXPERIMENT Pd1

grouping	=CHD	$=CD_2$	$-CH_2D$	$-CHD_2$	$-CD_3$
experimental	19.3	4.9	46.6	22.9	6.3†
calculated ($d = 0.20$)	20.0	5.0	48.1	23.8	3.1

† Assuming that the 9.0% in table 1 consisted of 4.9% $-CD_3$ in the alkene and 4.1% tertiary D in the alkane, see text.

MS analyses were obviously unreliable because of the overlap between the alkene and alkane spectra. On the other hand, the results for total D/alkane from the NMR analyses only agreed with the MS values for Pt1, Rh3 and Ir1. For all the other experiments, the MS results gave too high a value which indicated that the neglect of D_0- and D_1-alkane in the interpretation of the mass spectrometric results was not justified.

Further information about the exchanged alkenes is collected in the lower part of table 4. In all experiments there was preferential exchange of the methylene of the alkene, except over Pd which gave random exchange of all positions as already noted. Again, apart from Pd, the average deuterium content of the exchanged methylene and methyl groups of the alkenes were almost the same in each experiment. The number of groups, methylene or methyls, exchanged in each reacted alkene ranged between 1.2 and 1.5 with the higher values observed in the platinum runs at 295 K.

Further details about the distributions of deuterium in the alkane derived from the analyses are brought together in table 6. The average deuterium content of the exchanged methyl groups, D/CX_3, was calculated from the NMR spectra and when combined with the average primary deuterium content of the alkane gave the numbers of the different types of methyl groups shown in the table. The results for Rh2 can be used to illustrate these calculations. Values in table 1 show the relative amounts of primary D in the methyl groups CH_2D, CHD_2 and CD_3 were 26.3:21.7:18.8. It follows that the relative proportions of these groups were 26.3:21.7/2:18.8/3 and the average D content of the exchanged groups was 1.54.

TABLE 6. DISTRIBUTION OF DEUTERIUM IN THE ALKANES AND OTHER RESULTS FROM THE ANALYSES

experiment	Pt1 (LTR)	Pt2 (LTR)	Pt3 (LTR)	Pt4 (HTR)	Rh1	Rh2	Rh3	Ir1	Pd1
D/CX_3 in alkane	1.20	1.18	1.35	1.37	1.50	1.54	1.67	1.10	1.33
no. of groups									
$-CH_3$	1.90	2.02	1.88	1.80	1.89	1.88	1.70	1.97	1.86
$-CH_2D$	0.94	0.85	0.83	0.88	0.72	0.68	0.68	0.92	0.85
$-CHD_2$	0.10	0.08	0.18	0.20	0.23	0.28	0.37	0.11	0.21
$-CD_3$	0.06	0.05	0.11	0.12	0.16	0.16	0.25	—	0.08
exchanged D/alkane (g)	0.32	0.26	0.71	0.79	0.90	1.02	1.48	0.15	1.17
$2g/f$	17	7.2	16	7.2	35	50	—	(50)	1.5
addition/exchange (q)	3.8	2.4	2.0	0.9	3.6	5.1	—	(46)	0.1
% H in D_2	0.8	4.1	1.4	3.8	1.2	1.3	12.0	1.3	13.2

To account for the 1.72 primary D/alkane, the average number of exchanged groups per molecule was $1.72/1.54 = 1.12$ and thus the number of CH_3 groups was $3 - 1.12 = 1.88$. The exchanged D/alkane, g, was the extra deuterium present over and above the amount added in conversion of alkene to alkane, assuming that the chance of acquiring primary D was identical with the tertiary D found. For example in experiment Rh1 with primary and tertiary D/alkane of 1.67 and 0.77 atom/molecule respectively, the exchanged D/alkane was $0.90 = 1.67 - 0.77$. The next row in the table gives the ratio of exchanged D/alkane to the mean deuterium content of the alkene throughout the experiment, $2g/f$. This value provided a measure of the extent to which the deuterium content of the alkane was greater than that expected simply from the addition of two atoms to the alkenes. The fact that most values were significantly greater than 1.0 showed that either further exchange was occurring in the addition reaction or that the composition of the alkene that underwent conversion to alkane was richer in deuterium than the average for the total alkene, i.e. adsorbed and gas phase. The ratio q, which was obtained by dividing the percentage conversion to alkane by Φ, the mean number of deuterium atoms per 100 molecules of alkene, provided an approximate estimate of the relative ratio of addition to exchange. Finally, the % H in the deuterium at the end of each experiment was obtained by mass balance calculation.

Discussion

The results in table 3 show that for the conversion of 2-methylpropene to alkane at 235 K the relative activities of the metals were Rh > Ir > Pd > Pt, but the spread of activity was only a factor of about 20. The lower rate for Pt2 in comparison with Pt1 was consistent with an approximate first-order dependence of rate on the pressure of deuterium. The reduction of rate by a factor of only 13 at 295 K from Pt3 (LTR) to Pt4 (HTR) showed that strong metal-support interactions were not causing a very marked change in the catalytic properties of the platinum and the differences in the character of the reactions, as shown by the various results in tables 1, 4, 5 and 6 were also minimal.

Comparisons can be made between the present results for the reactions of 2-methylpropene with information in the literature for the reactions of other alkenes, such as ethene and propene, on the same four metals. Bond & Wells (1964) gave details for the reactions of both ethene and propene with deuterium over a number of supported metals, including those used in this work. Exchange was found to be faster than addition with palladium and considerable dilution of the surface deuterium with hydrogen occurred so that appreciable amounts of alkanes containing less than two deuterium atoms were formed. Our results with palladium conform to this behaviour. Likewise, there is agreement that iridium gives the smallest rates of exchange to addition with all three alkenes and that rhodium shows rather more exchange than platinum.

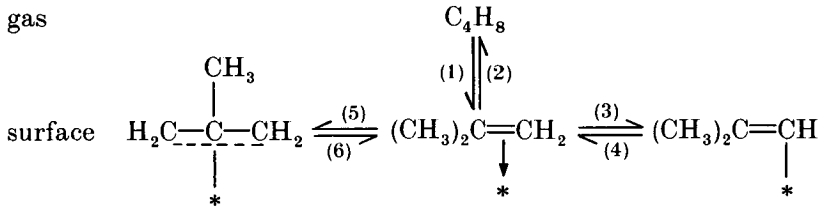
The earlier work reviewed by Bond & Wells (1964) interpreted the results with ethene and propene solely in terms of associative mechanisms, but considerable evidence published since then has indicated the importance of dissociative mechanisms for the exchange and isomerization of propene and larger alkenes

(Hironaka *et al.* 1966; Ueda & Hirota 1970; Touroude *et al.* 1974; Touroude & Gault 1974; Ledoux *et al.* 1978; Ledoux *et al.* 1980). We believe it is necessary to consider the various possible types of reaction that might occur with the 2-methylpropene/2-methylpropane system before attempting to interpret the present results.

Possible mechanisms

As there are a number of possibilities it is desirable to review dissociative and associative processes separately and to examine the consequences of each type of reaction for alkene exchange or the conversion of alkene to alkane.

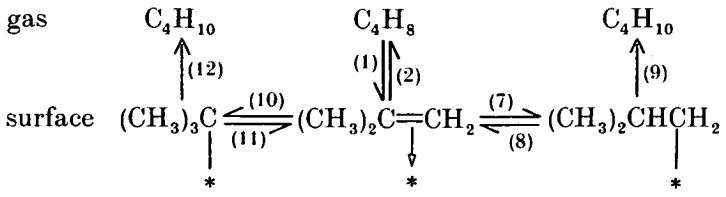
Either of the dissociative reactions shown in scheme 1 might contribute to alkene exchange. Steps (1) and (2) combined with (3) and (4) would give replacement of one or both of the hydrogen atoms in the methylene group of the alkene, but no exchange in the methyl groups. Complications from isotope effects have to be considered at the temperatures used for the experiments. Results previously published, Flanagan & Rabinovitch (1956) and John *et al.* (1976), show that the rate of dissociation of C—H bonds occurs at least a factor of 10 more rapidly than the corresponding reaction for C—D bonds at temperatures such as 235 K. Thus, repetition of steps (3) and (4) will lead to a greater proportion of $(CH_3)_2C{=}CD_2$ than would be expected if random replacement occurred without any kinetic isotope effect.



SCHEME 1. Possible dissociative reactions that may contribute to the exchange of 2-methylpropene.

Steps (1) and (2) combined with (5) and (6) would lead initially to exchange in a methyl group, but subsequently to the replacement of any of the eight hydrogen atoms in the alkene. Steps (5) and (6) can also provide a means of double-bond movement without further exchange by loss and gain of an H atom; this type of reaction will be relatively rapid because of the isotope effect.

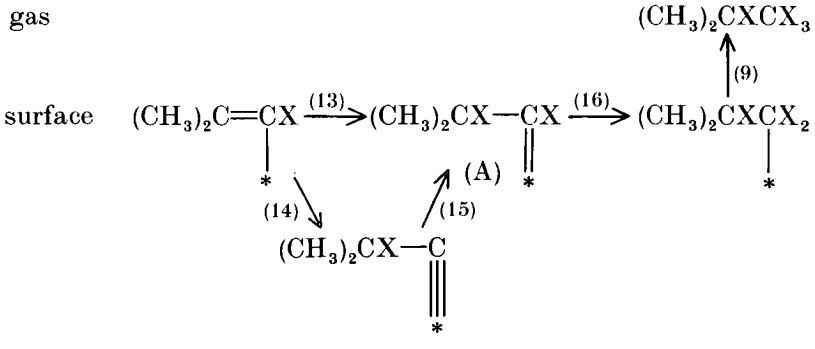
In the associative reactions, shown in scheme 2, steps (7) and (8) lead neither to exchange of the alkene nor do they provide a means of obtaining enhanced exchange of the alkane over and above the simple addition corresponding to steps (7) and (9). The combination of steps (1) and (2) with (10) and (11) can give alkene exchange, initially in either the methylene group or the methyl group, but subsequently in all positions, so that the overall results should be similar to those described for the dissociative mechanism involving steps (5) and (6) in scheme 1. Steps (10) and (11) can also contribute to further exchange of the alkane to give products containing more deuterium than expected just from the addition steps (10) and (11). However, unless there is some degree of restricted rotation of the 2-



SCHEME 2. Associative reactions of 2-methylpropene that provide routes to alkane and might contribute to exchange of alkene by steps (10) and (11).

alkyl species formed by step (10) further exchange associated with the repetition of steps (10) and (11) would be spread over the three methyl groups of the alkane and not concentrated in one such group. Other mechanisms have to be considered to account for the experimental results that, as we shall see, show that the additional exchange of the alkane tends to be concentrated in a single methyl group.

It is likely that the most highly exchanged methyl group in the alkane derives from the methylene group of the alkene and two possible ways for this to happen are shown in scheme 3. Step (13) involves an acquisition of an atom (H or D) at the central carbon atom of the adsorbed vinyl species to form intermediate A. The alternative route gives an alkylidyne species by isomerization of the vinyl in step (14) and then conversion to A through step (15). Further reaction of A by step (16) leads to the 1-alkyl adsorbed intermediate which will then form an alkane with enhanced exchange in one methyl group.



SCHEME 3. Possible routes from vinyl to alkyl intermediates leading to enhanced exchange of one methyl group of the alkane. X represents H or D.

Deuterium distributions and choice of mechanisms

Platinum and rhodium

Both these metals showed preferential exchange, more marked at lower temperatures, in the methylene group of the alkane. Another important feature of the results in table 4 is that the extent of the exchange in the methyl groups which had acquired deuterium was identical with the extent of the exchange in the methylene group. These results give a strong indication that the principal mechanisms are exchange through the vinyl dissociative route, steps (3) and (4),

combined with an isomerization that converts the methylene group into a methyl group through H atom transfer via the π-allyl intermediate. This isomerization must be mainly intramolecular in that the H atom dissociated is the H atom acquired and further exchange does not occur to an appreciable extent.

The values of M, which ranged from 1.2 to 1.6, were higher for rhodium than platinum and tended to be larger with increase of temperature. It follows that step (3) cannot be much faster than (2) because of the limited extent of multiple exchange. The results in table 4 also demonstrate that the majority of the exchanged alkene molecules possessed either an exchanged methylene group or an exchanged methyl group, except for the higher-temperature results with platinum where the number of exchanged groups per molecule increased to 1.4 or 1.5. These facts are in accord with the mechanisms suggested.

Addition to form alkane, see table 6, was noticeably faster than exchange on rhodium and on platinum, except for the special case of platinum at 295 K subjected to HTR. But the most striking feature of the results was the evidence that alkane formation was accompanied by further exchange which was mainly concentrated in one methyl group as shown by the results in table 6. Significant amounts of $—CD_3$ groups were detected in the alkanes formed over rhodium and to a lesser extent with platinum and the average number of exchanged methyl groups per alkane was usually in the range from 1.0 to 1.2, rising only to 1.3 in the special case (Rh3) where all the alkene had been converted to alkane. These results are not consistent with alkyl reversal, steps (10) and (11), as the mechanism for the exchange accompanying addition. Such a mechanism would tend to exchange more of the methyl groups to a limited extent rather than one methyl group to a marked degree unless there was some measure of restricted rotation of the adsorbed 2-alkyl species such that repeated exchange of a single group was favoured. We prefer to think in terms of the other mechanisms outlined in scheme 3 as the means whereby the further exchange associated mainly with one methyl group of the alkane is achieved. Rhodium is known to be somewhat better than platinum at forming αα-diadsorbed species from hydrocarbons (Kemball 1959; Brown *et al.* 1988) and so it is not surprising that it shows the greater amount of further exchange associated with alkane formation even at comparatively low temperatures.

Our conclusions about the mechanisms for the reactions of 2-methylpropene differ from those given by Naito & Tanimoto (1987) for the reactions of propene over Pt/SiO_2. They suggested that dissociative mechanisms operated only in the absence of added hydrogen or deuterium, i.e. for reactions such as the exchange between C_3H_6 and C_3D_6. We believe that dissociative mechanisms are essential to account for our results with 2-methylpropene. They argued for exchange by an associative mechanism in the reaction of C_3H_6 with D_2 on the grounds that both exchange and addition had the same activation energy and the same kinetics. But to explain the selective nature of the exchange they were forced to assume that the two methyl groups in the 2-alkyl intermediate were not identical. We suggest that the identity of activation energies and kinetics for exchange and addition may be a coincidence and that the preferential exchange of various vinyl hydrogens in propene arises through dissociative mechanisms and not from some restricted

rotation of the 2-alkyl intermediate in an associative mechanism. The small extent of exchange in the methyl group of the propene observed by Naito & Tanimoto is difficult to explain if an associative mechanism operates. On the other hand, we agree with them on the need to have an intramolecular mechanism for isomerization to account for the changes in the distribution of deuterium atoms in the propene molecules as reaction proceeds.

Iridium

The rate of exchange was small and exchanged alkene was not formed in sufficient quantity for NMR analysis. The results in tables 2 and 6 show that the major product of the addition reaction was D_2-alkane but a small amount of further exchange also occurred and, as with rhodium and palladium, this was confined to one methyl group of the alkane.

Palladium

The results with palladium differed substantially from those with the other metals. The exchange reaction was 10 times faster than the addition process. The distribution of deuterium in the alkene was random apart from a slight excess of $-CD_3$ presumably as a consequence of the kinetic isotope effect. Either of the mechanisms leading to random distributions, i.e. π-allyl through steps (5) and (6) or alkyl reversal through steps (10) and (11), might be operating and a choice has to be made on other grounds. An important point is that, with palladium, the amount of deuterium in the alkane was close to the value expected for addition of two atoms to the alkene without further exchange, as shown by the value of $2g/f$ in table 6. This suggests that alkyl reversal may be less important than the π-allyl mechanism for the exchange of the alkene. The efficient exchange of the alkene implies that step (2), alkene desorption, is a relatively fast reaction over palladium. The ease of alkene desorption is, of course, one of the factors which makes palladium a good catalyst for the selective hydrogenation of alkynes. The rapid exchange that occurred with palladium led to the most substantial dilution of the surface pool with hydrogen so that the chance of acquiring a D atom was only 0.35. Desorption of H_2 and HD must be relatively slow reactions because a comparison of the results in tables 4 and 6 show that the chance of acquiring a D atom, measured by the amount of tertiary D in the alkane, was less than expected from the composition of the hydrogen/deuterium gas. This observation applied to most of the results with rhodium and platinum as well as for palladium. Naito & Tanimoto (1986) showed that exchange was faster than addition for the reaction of propene and deuterium over Pd/SiO_2 and they found that selective exchange was followed by an intramolecular double-bond migration leading to a more random distribution in the alkene. Our results with 2-methylpropene are broadly similar to their findings with propene but, as indicated above, we are doubtful about the emphasis that they place on associative mechanisms for the exchange of the alkene.

Conclusions

A number of conclusions can be made from these investigations.

1. Deuterium NMR spectroscopy is a good technique for use with the 2-methylpropene/deuterium system. The detailed information, so obtained, on the distribution and grouping of deuterium atoms in the products is helpful in identifying intermediates and mechanisms for the reactions on metal catalysts.

2. Palladium shows a preference for exchange of alkene rather than addition and leads to a random distribution of the deuterium in the alkenes.

3. Addition is much faster than exchange with iridium and somewhat faster with rhodium and platinum.

4. Clear indications of a role for exchange through a dissociative mechanism involving adsorbed vinyl intermediates are found from the distribution of products over rhodium and platinum.

5. Double-bond migration through an intramolecular π-allyl mechanism is also important and exchange through a π-allyl mechanism is indicated for palladium.

6. Further deuterium is introduced, largely into one methyl group, when alkene is converted to alkane, over iridium, platinum and particularly rhodium. Mechanisms other than the usual alkyl reversal processes are required to account for these results.

The NMR spectra were obtained through the SERC high field facility in Edinburgh. C.K. holds a Leverhulme Emeritus Fellowship.

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Exchange Reactions of Alkanes containing Quaternary Carbon Atoms over Supported Metal Catalysts

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A comparison has been made of the exchange reactions with deuterium of 2,2-dimethylpropane (DMP), 2,2,3,3-tetramethylbutane (TMB) and 2,2,4,4-tetramethylpentane (TMP) over supported catalysts containing iridium, palladium, platinum or rhodium at temperatures in the neighbourhood of 400 K. Reactions were followed mass-spectrometrically and products were also examined by deuterium n.m.r. spectroscopy. Four processes or mechanisms were found to contribute to different extents with the various hydrocarbon–metal systems. These were (I) stepwise exchange, (II) methyl-group exchange, and more general multiple exchange involving (III) $\alpha\gamma$-diadsorbed or (IV) $\alpha\delta$-diadsorbed intermediates. Some isomerisation of TMP was observed to occur simultaneously with exchange with the TMP–rhodium system.

he study[1-3] of exchange reactions of alkanes with deuterium has yielded much evidence bout the nature and reactivity of adsorbed intermediates and so supplied information hich is fundamental to an understanding of the mechanisms of hydrocarbon reactions n metals. Recently, the use[4-6] of high-field deuterium n.m.r. spectroscopy has provided means of identifying the groupings of deuterium atoms in the products of exchange eactions and of estimating the distribution of the atoms in the various groupings. esults, so obtained, are more revealing than those from the traditional mass- pectrometric technique and have necessitated a revision of some of the accepted ideas bout the mechanisms of exchange reactions.[5,6] With linear or slightly branched ydrocarbons, very extensive multiple exchange is observed on many metal catalysts but ith molecules such as 2,2-dimethylpropane (DMP), the quaternary carbon atom estricts the number of possible intermediates that can be formed and limits the types of ultiple exchange that can occur.

The purpose of the present work was to compare the behaviour of the hydrocarbons MP, 2,2,3,3-tetramethylbutane (TMB) and 2,2,4,4-tetramethylpentane (TMP) in eactions with deuterium on supported iridium, palladium, platinum and rhodium atalysts. Studies over a period of years[6-11] with DMP have shown that the exchange of is molecule with deuterium may occur by one or more of three processes. The first of ese, process I, involves stepwise exchange through the reversible formation of an dsorbed alkyl radical. Process II gives multiple exchange, but limited to a single methyl roup through interconversion between adsorbed alkyl and α,α-diadsorbed (alkylidene) pecies. Process III, which becomes significant only at higher temperatures, leads to the rmation of initial products containing deuterium atoms in two or more methyl groups; requires the interconversion of adsorbed alkyl radicals and $\alpha\gamma$-diadsorbed species. In ontrast to the number of studies with DMP, relatively little work has been carried out ith TMB and TMP. The interest in TMB concerns the possibility of multiple exchange rough $\alpha\delta$-diadsorbed intermediates. Such species are needed to allow the multiple xchange to propagate beyond the three methyl groups attached to one of the two entral carbon atoms. Maier and his colleagues have reported results on the exchange

of TMB on platinum[12] and rhodium[13] but in neither case were extensively exchange initial products detected. On the other hand, preliminary work[14] with a silica-supporte rhodium catalyst has shown evidence for an exchange process involving $\alpha\delta$-adsorbe intermediates. With TMP as reactant extensive multiple exchange might occur throug the formation of $\alpha\gamma$-adsorbed intermediates if reversible dissociations of C—H bonc both in the methyl groups and the central methylene group were possible. Formation c $\alpha\gamma$-species involving the central group would allow the exchange process to propagat over the whole molecule. Alternatively, if the exchange of the methylene group wa unlikely either for steric reasons or from the intervention of isomerisation reactions the the only means of achieving multiple exchange extending beyond three methyl group with TMP would be through $\alpha\varepsilon$-diadsorbed intermediates. Such species have bee shown to play an important part in dehydrocyclisation reactions with TMP and othe alkanes on sintered metal films.[15] The sintering of the films had the effect of reducing th rate of the exchange reactions so that processes such as isomerisation an dehydrocyclisation could be studied in the presence of deuterium without complicatior from exchange. We hoped that a comparative study of the behaviour of DMP, TMB an TMP in exchange reactions would provide clear evidence of the relative importance c $\alpha\gamma$-, $\alpha\delta$- and $\alpha\varepsilon$-intermediates on the four supported metal catalysts.

Experimental

The preparation and pretreatment of the platinum and rhodium catalysts whic contained 10^{-4} mol metal g^{-1} silica have been described.[16] The palladium catalys donated by I.C.I., contained 2.5×10^{-6} mol Pd g^{-1} calcium aluminate and was pretreate in a similar manner to the previous catalysts. The iridium catalyst, with 2×10^{-5} mc metal g^{-1} γ-alumina, has also been described and characterised.[17] The DMP (99%) an deuterium (99.5%) were supplied by the Matheson Co. and the TMB (99%) wa obtained from the Aldrich Chemical Co. Ltd. Prof. J. K. A. Clarke gave us a sample c TMP, an API standard sample as used in the study with sintered films.[15] No furthe purification of the hydrocarbons was attempted apart from a freeze–thaw cycle prior t each experiment. The deuterium was diffused through a heated palladium–silver allo thimble.

Two types of apparatus were used (a static system and a recirculation system) an each was connected by a capillary leak to a Vacuum Generators Micromass 601 mas spectrometer. Most of the experiments with DMP and TMB were carried out in th static system[10] which had a volume of 240 cm^3. The usual mixture for runs which wer not to be analysed subsequently by n.m.r. spectroscopy was 8:1 of deuterium hydrocarbon and a pressure of hydrocarbon of 693 Pa, giving 3.5×10^{19} molecules in th reaction vessel. For runs to be examined by deuterium n.m.r. spectroscopy a large charge of hydrocarbon was needed (4.3 kPa, equivalent to 2.0×10^{20} molecules) and th deuterium hydrocarbon ratio was 5:1. All experiments with TMP were carried out in th recirculation apparatus (1270 cm^3) using an 8:1 ratio of deuterium:hydrocarbon and hydrocarbon pressure of 733 Pa which gave 2.1×10^{20} molecules in the apparatus. Th larger circulation system was necessary for runs with TMP because the vapour pressur was insufficient to give enough material in the static apparatus for subsequent analysi by n.m.r. spectroscopy.

The course of the exchange reactions for all three hydrocarbons were followed usin the amounts of the pseudoparent ions formed by loss of a methyl group from th molecules in the mass spectrometer using 35 eV† electrons to bring about ionisation. Th usual corrections were made for naturally occurring isotopes and for fragmentation t other ions. In addition, a further small but important correction had to be made wit

† 1 eV = 0.1602177 aJ.

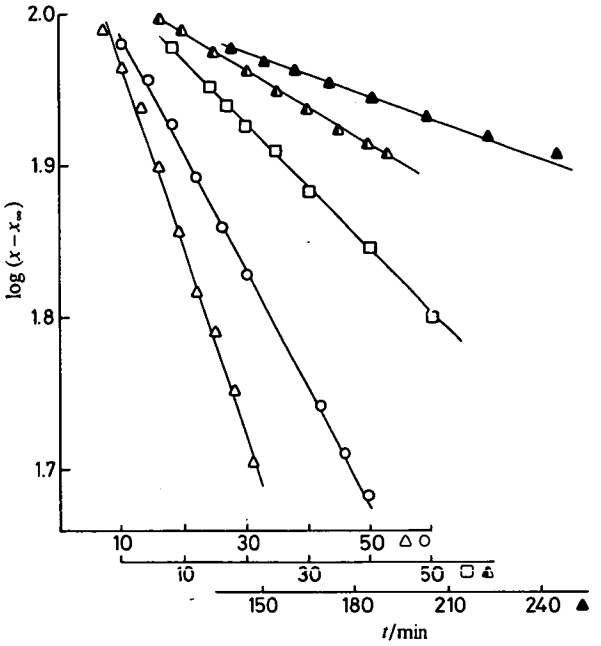

Fig. 1. Rate plots according to eqn (1) for reactions over iridium (▲, ○), palladium (▲) and platinum (△, □): squares, DMP; circles, TMB; triangles, TMP.

TMB and TMP associated with the formation of parent ions. With TMB, the peak at $m/e = 114$ had to be corrected for the parent ion $C_8H_{18}^+$, amounting to 0.28% of the pseudoparent ions, to obtain the contribution from $C_7D_{15}^+$. The corresponding correction with TMP for the presence of $C_9H_{20}^+$ amounted to 1.25% of the pseudoparent ions and was subtracted from the peak at $m/e = 128$ to find the contribution from $C_8H_2D_{15}^+$.

Standard methods[1] were used to obtain the initial rates of exchange and the mean number of deuterium atoms, M, in the pseudoparent ions from the initial products. For each run, the results were plotted according to the reversible first-order equation for the disappearance of the light pseudoparent ions ($C_4H_9^+$, $C_7H_{15}^+$ or $C_8H_{17}^+$, respectively, for DMP, TMB and TMP)

$$-\ln(x-x_\infty) = kt/(100-x_\infty) - \ln(100-x_\infty) \qquad (1)$$

in which x is the percentage of the light ion at time t, x_∞ (≈ 0) is the value at equilibrium and k is the initial rate (in % time^{-1}).

The technique for collecting the hydrocarbon samples and for analysing them subsequently by deuterium n.m.r. spectroscopy has been described.[5]

Results

Kinetic Behaviour

Experiments with the iridium, platinum or rhodium catalysts were carried out at *ca.* 393 and 423 K but temperatures up to 460 K were needed to obtain adequate rates with the palladium catalyst because of its low loading of metal.

Runs with iridium, palladium or platinum conformed to the first-order reversible rate equation (1) as indicated by the representative plots in fig. 1; a slight decrease in rate was apparent for the experiment with TMP on palladium at 456 K but only after 250 min.

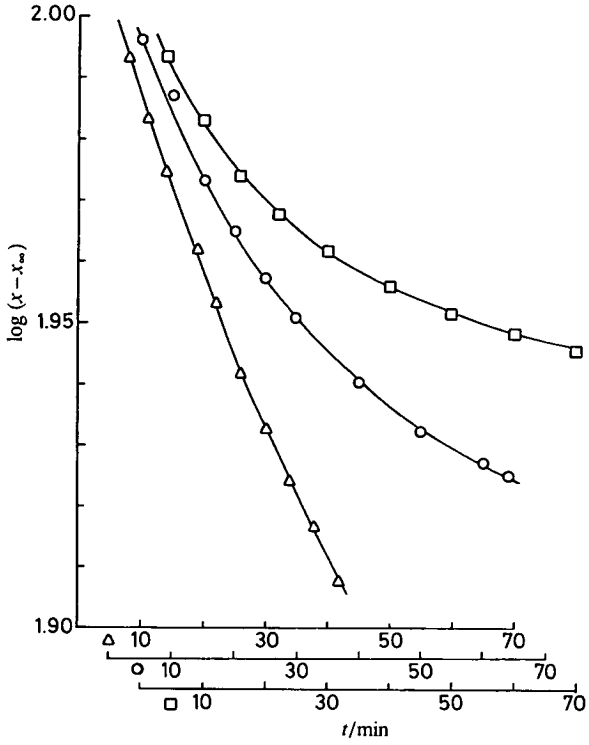

Fig. 2. Rate plots according to eqn (1) for reactions over Rh–SiO_2 at 423 K: (□) DM (○) TMB, (△) TMP.

However, the rates of exchange reactions using rhodium decreased with time, see fig. and the effect was most pronounced with DMP and least noticeable with TMP.

Initial rates for all the exchange reactions are given in the Arrhenius diagram for eac metal in fig. 3. Similar rates of reaction were found with the three hydrocarbon particularly over palladium which gave results close to a common Arrhenius line wit activation energy 91 ± 4 kJ mol^{-1}. The line given for rhodium is based on previous data for the exchange of TMB and corresponds to an activation energy of 54 kJ mol Likewise for iridium the line is parallel to that found[11] for exchange of DMP over th temperature range 301–452 K with $E = 38$ kJ mol^{-1}. With platinum, the line drawn giv an activation energy of 103 ± 13 kJ mol^{-1} but this value is higher than the activatio energy of 56 kJ mol^{-1} reported for an alumina-supported platinum catalyst.[11]

Product Distributions

For each exchange experiment the product distributions in terms of the pseudoparen ions were obtained from the mass-spectrometric analyses at low conversions and th kinetic data were used[1] to calculate M the mean number of D atoms in the ions fro the initial products. Results for palladium are given in the upper part of table 1. Th values of M at both temperatures for DMP and for TMB at 424 K showed that stepwis exchange was the dominant process with these systems. This conclusion was confirme by the agreement between the observed product distributions at 10 % conversion and th calculated random distributions. With TMP at 456 K, stepwise exchange was again th main type of reaction but there was a contribution from some other process as well.

Results for platinum and iridium are given in table 2 at a slightly greater conversio

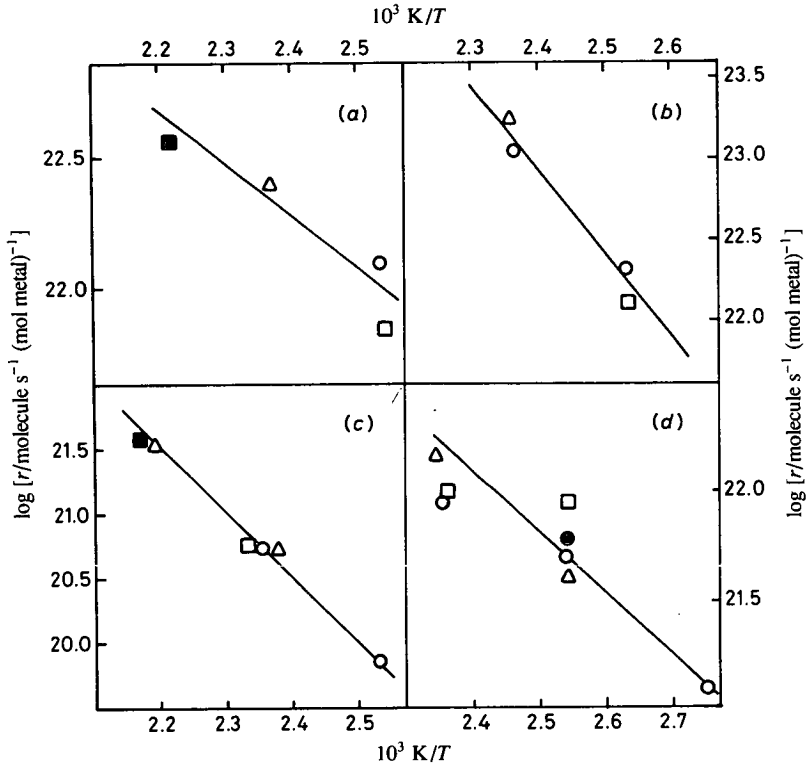

Fig. 3. Rates of exchange plotted on Arrhenius diagrams for (*a*) iridium, (*b*) platinum, (*c*) palladium and (*d*) rhodium: squares, DMP; circles, TMB; triangles, TMP. Filled symbols were rates from experiments on the static line planned for n.m.r. with the higher pressure of hydrocarbon and a 5:1 ratio of D_2:hydrocarbon.

of 15%. This value was chosen in order to show the small amounts of the more highly exchanged products. At 15% conversion there is a significant contribution from molecules that have made two effective visits to the catalyst surface: about 14% of the molecule will have exchanged once and 1% will have reacted twice. With iridium, some multiple exchange limited to methyl groups, *i.e.* process II, occurs with all three reactants but further multiple exchange contributes only to a very small extent. General multiple exchange plays a greater part in the reactions over platinum and increases with temperature as shown by the two sets of results with TMB. Results for reactions over rhodium at 10% conversion are given in table 3 and show significant contributions from multiple exchange processes. The influence of temperature on the values of M for exchange over iridium, platinum and rhodium catalysts are shown in fig. 4.

N.M.R. Analyses

DMP

The main features associated with the deuterium n.m.r. spectra of exchanged DMP have been established.[5,6] The chemical shift for the $-CH_2D$ group occurs at $\delta = 0.918 \pm 0.007$ ppm. The groupings $-CHD_2$ and $-CD_3$ are easily recognised because each additional deuterium atom gives rise to an α-shift of -20.7 ppb and the resonances are well separated. For highly exchanged products, such as those formed over rhodium catalysts,

Table 1. Product distributions for exchange on palladium

reactant...	DMP		TMB		TMP
temp./K...	429	460	424		456
MS distribution of ions at 10% conversion		calc. A		calc. B	
D_1	9.54	(9.51)	9.33	9.46 (9.52)	9.05
D_2	0.43	(0.45)	0.64	0.52 (0.47)	0.62
D_3	0.03	(0.01)	0.03	0.02 (0.01)	0.11
$\geqslant D_4$	—	—	—	— —	0.03
M	1.00	—	1.03	1.03 —	1.16
conversion for n.m.r. analyses...	—	—	20.3	— —	19.8
%D in groupings		calc. C		calc. D	
$-CH_2D$		(95)	93	(97)	88
$-CHD_2$		(5)	7	(3)	6
$-CD_3$			—		3
$-CD_3 + \gamma$ shifts			—		3

The calculated distributions A and B, for the pseudoparent ions are those expected for stepwise exchange at 10% conversion for 9 and 15 exchangeable H atoms. Distribution C corresponds to a random distribution with a chance $d = 0.0256$ of a D atom in each position based on the mass spectrometrically determined average D-content of the $C_4X_9^+$ ions of 0.231. Distribution D corresponds to a random distribution with a chance $d = 0.0165$ of a D in 15 positions based on the mass spectrometrically determined average D-content of the $C_8H_2X_{15}^+$ ions of 0.248.

Table 2. Product distributions for exchange on platinum and iridium at 15% conversion

catalyst...	platinum				iridium		
reactant...	DMP	TMB		TMP	DMP	TMB	TMP
temp./K...	394	395	423	424	392	394	422
composition of ions							
D_1	10.30	8.69	6.12	4.99	12.78	11.22	12.01
D_2	2.66	3.25	3.03	2.91	1.86	2.74	2.03
D_3	1.30	1.45	1.52	1.79	0.32	0.67	0.42
D_4	0.44	0.73	1.08	1.28	0.04	0.12	0.16
D_5	0.18	0.32	0.78	0.98	—	0.03	0.09
D_6	0.08	0.19	0.60	0.74	—	0.02	0.06
D_7	0.04	0.11	0.43	0.59	—	0.01	0.06
D_8	0.03	0.08	0.35	0.49	—	0.01	0.06
D_9	0.02	0.07	0.30	0.41	—	0.05	0.06
D_{10}	—	0.04	0.26	0.32	—	0.02	0.06
D_{11}	—	0.03	0.19	0.19	—	0.02	—
D_{12}	—	0.03	0.15	0.16	—	0.04	—
D_{13}	—	0.01	0.11	0.11	—	0.02	—
D_{14}	—	0.00	0.07	0.04	—	0.01	—
D_{15}	—	0.00	0.00	—	—	0.02	—
M	1.45	1.75	2.24	2.64	1.11	1.35	1.27

Table 3. Product distributions for exchange on rhodium at 10% conversion

reactant...	DMP		TMB		TMP	
temp./K...	393	423	394	424	393[a]	426
composition of ions						
D_1	6.80	4.18	6.47	4.82	6.24	4.32
D_2	1.30	1.35	1.22	1.13	1.17	1.13
D_3	0.95	1.29	0.42	0.51	0.49	0.62
D_4	0.36	0.72	0.14	0.17	0.25	0.39
D_5	0.18	0.51	0.05	0.15	0.25	0.43
D_6	0.12	0.44	0.03	0.14	0.21	0.36
D_7	0.10	0.44	0.04	0.18	0.21	0.43
D_8	0.10	0.52	0.09	0.29	0.33	0.61
D_9	0.10	0.55	0.22	0.31	0.25	0.51
D_{10}	—	—	0.12	0.38	0.18	0.45
D_{11}	—	—	0.13	0.40	0.21	0.42
D_{12}	—	—	0.28	0.50	0.13	0.20
D_{13}	—	—	0.16	0.41	0.05	0.10
D_{14}	—	—	0.25	0.42	—	—
D_{15}	—	—	0.35	(0.18)[b]	—	—
M	1.51	(3.2)[b]	3.79	(4.6)[b]	2.50	3.54

[a] The ratio of D_2:hydrocarbon in this experiment was 5:1 compared with 8:1 in the others.
[b] Values which were subject to greater error.

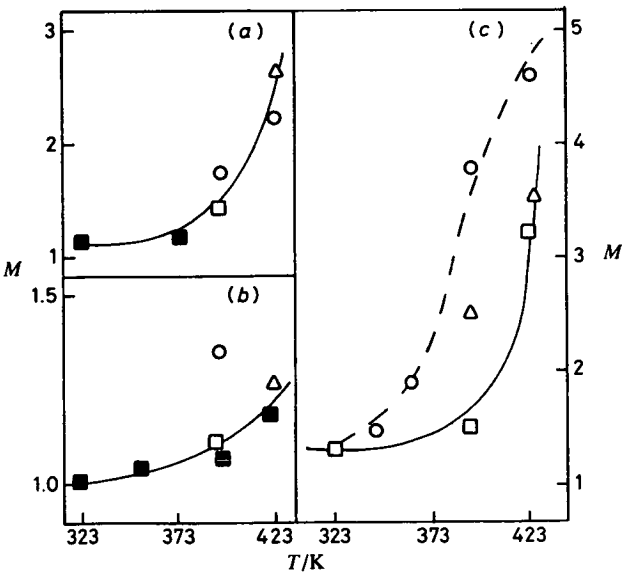

Fig. 4. Influence of temperature on the values of M, measuring the multiplicity of exchange, for reactions on (*a*) platinum, (*b*) iridium and (*c*) rhodium catalysts: squares, DMP; circles, TMB; triangles, TMP. Filled symbols are results obtained previously for DMP on platinum[5,10] or iridium.[18]

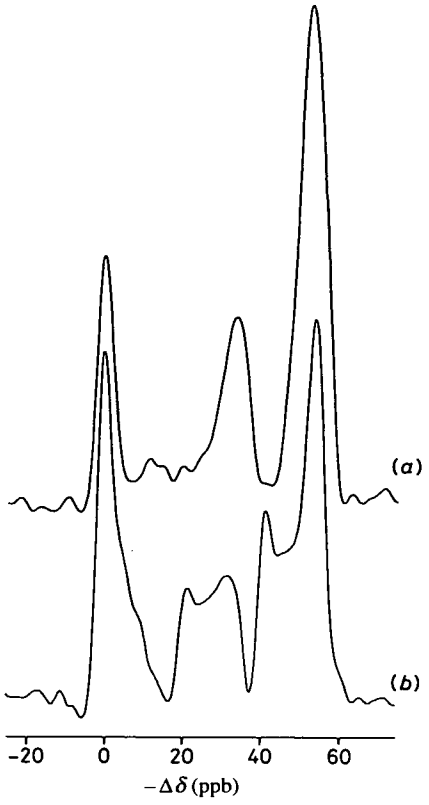

Fig. 5. N.m.r. spectra for DMP and TMB exchanged over rhodium: (*a*), TMB 15.9% reacted at 424 K using 5:1 ratio of D_2:hydrocarbon and highest-frequency peak at $\delta = 0.869$ ppm; (*b*), DMP 12% reacted at 423 K using 8:1 ratio of D_2:hydrocarbon with highest-frequency peak at $\delta = 0.924$ ppm with respect to TMS.

additional peaks are found corresponding to the groupings $-CHD_2$ and $-CD_3$ in molecules which are substantially exchanged in the other methyl groups as well. The position of these resonances are influenced by γ isotopic shifts due to the deuterium atoms in the other methyl groups. Even though the individual γ shifts are small, the combination of a number of them leads to a total shift which is sufficient to enable a separate resonance to be detected. An example of such a spectrum is shown in fig. 5(*b*); the separation between the two peaks for the $-CHD_2$ groupings is -10.2 ppb and that for the two peaks for $-CD_3$ is -12.7 ppb. A comparison of this and other spectra with the relevant mass-spectrometric analyses indicated that the value for each γ-shift was *ca.* -1.7 ppb.

TMB

The chemical shift for the $-CH_2D$ was $\delta = 0.865 \pm 0.007$ ppm, and spectra of the products from three reactions are shown in fig. 5–7. Small peaks from the spectra from the rhodium experiments indicated that the α-shift was *ca.* -20 ppb and the total shifts for the highly exchanged molecules were -53.4 and -55.1 ppb. If the two α shifts accounted for -40 ppb of these displacements the remaining -14 ppb represented the combined effect of up to six γ and nine δ shifts.

The spectrum of the relatively highly exchanged sample from the reaction over platinum at 423 K, fig. 6, shows just three slightly broadened resonances corresponding

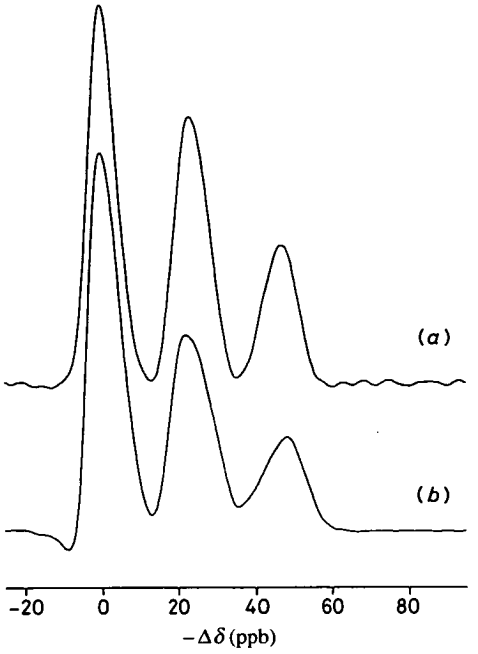

Fig. 6. N.m.r. spectra for TMB and TMP substantially exchanged over platinum: (*a*), TMP 49.3% reacted at 424 K and highest-frequency peak at $\delta = 0.983$; (*b*), TMB 70.3% reacted at 423 K with highest-frequency peak at $\delta = 0.868$ with respect to TMS.

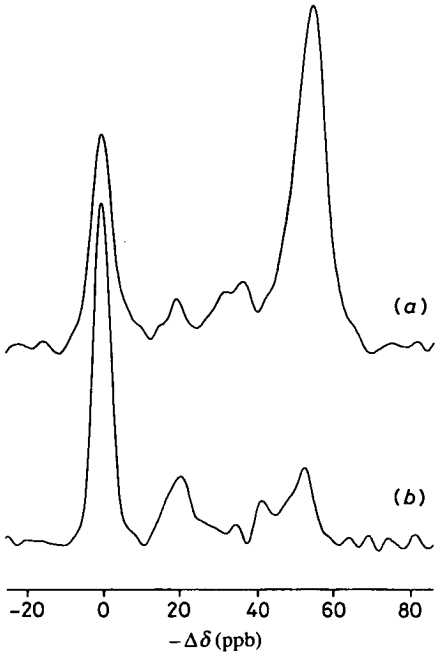

Fig. 7. N.m.r. spectra for TMB and TMP exchanged over rhodium: (*a*), TMB 13.7% reacted at 393 K using a 4:1 ratio of D_2:hydrocarbon and highest-frequency peak at $\delta = 0.858$ ppm; (*b*), TMP 15.9% reacted at 394 K using a 5:1 ratio of D_2:hydrocarbon with the highest-frequency peak at $\delta = 0.983$ with respect to TMS.

Table 4. Distributions of deuterium atoms in the methyl groups in the products from reactions over platinum and iridium

Catalyst	platinum			iridium
reaction...	DMP	TMB	TMP	TMP
temp./K...	431	423	424	422
% conversion...	14.4	70.3	49.3	19.0
M_x[a]	1.86	3.24	3.43	1.58
grouping	percentage of total deuterium			
$-CH_2D$	63	50	44	91
$-CHD_2$	25	34	37	9
$-CD_3$	12	16	19	0

[a] M_x is the mean number of deuterium atoms in the pseudoparent ions from exchanged molecules.

to $-CH_2D$, $-CHD_2$ and $-CD_3$ groups. The isotopic shifts associated with the latter peaks were -22.4 and -48.5 ppb and so they correspond to the usual α shifts together with small contributions from the minor γ and δ shifts.

TMP

The chemical shift for primary deuterium in TMP was 0.979 ± 0.007 ppm. A spectrum using the naturally occurring deuterium in the molecules showed that the chemical shift for deuterium in the methylene group was 1.24 ppm, but no exchange was detected in this position in any of the reactions. Spectra of products from exchange over palladium and iridium showed that the α-shift for the grouping $-CHD_2$ was -20.7 ppb, a value identical to that found for DMP. A spectrum for substantially exchanged TMP over platinum is shown in fig. 6 and gave the usual resonances for $-CH_2D$, $-CHD_2$ and $-CD_3$ with some contributions from minor isotopic shifts as the displacements were -23.2 and -46.7 ppb.

Part of the spectrum for TMP reacted over rhodium is shown in fig. 7, but two small peaks containing 7% of the total deuterium observed by n.m.r. were also present with chemical shifts of 1.445 and 1.484 ppm. In a second experiment using rhodium, 6% of the deuterium was associated with a small peak at 1.438 ppm. These results show unequivocally that exchange over rhodium was accompanied by other reactions such as isomerisation with the peaks in the region of $\delta = 1.45$ ppm representing secondary (or tertiary) deuterium atoms in the products. Since the isomerised products were likely to contain primary deuterium atoms as well they probably contributed to some of the small peaks in the spectrum, shown in fig. 7, which was therefore not attributable solely to primary deuterium in exchanged TMP.

Distributions of Primary Deuterium Atoms in Products

Results for the distributions of the deuterium atoms in different groupings for products from reaction over palladium are given in the lower part of table 1. Corresponding results for reactions over platinum and iridium are shown in table 4 and the more detailed analyses made for rhodium are presented in table 5.

Table 5. Distributions of deuterium atoms in the methyl groups in the products from reactions over rhodium

reactant...	DMP	TMB		TMP
temp./K...	423	394[a]	423	394
% conversion...	12.0	13.7	15.9	15.9
M_x[b]	3.18	2.98	4.63	2.61
grouping	percentage of total deuterium			
$-CH_2D$	22.6	25.8	16.4	53.5
$-CH_2D$ + minor shifts	7.2	1.3	4.6	—
$-CHD_2$	8.6	3.6	2.0	16.5
$-CHD_2$ + minor shifts	12.8	4.5	23.0	1.4[c]
$-CD_3$	13.3	6.6	0.0	5.8
$-CD_3$ + minor shifts	35.5	58.2	54.0	15.7[c]
	100.0	100.0	100.0	92.9[d]

[a] The D_2:hydrocarbon ratio was 4:1 in this experiment. [b] M_x is the mean number of deuterium atoms in the pseudoparent ions from exchanged molecules. [c] These percentages probably include some primary deuterium atoms from isomerised products. [d] Some 7% of the total deuterium was present as secondary or tertiary atoms in isomerised products.

Discussion

Reactions other than Exchange

The work of Finlayson *et al.*[15] has shown that TMP will undergo cyclisation or isomerisation on sintered films of iridium, palladium, platinum or rhodium at temperatures only slightly greater than those used in the present investigation. Sintered films proved useful for their purpose which was to observe the deuterium content of the products from the other reactions without the complications from too much exchange of TMP. The supported catalysts we used appear to have given us the results we wanted, *i.e.* exchange without other reactions, except in the case of rhodium. The presence of some 6–7% of the total deuterium in the products from the TMP–rhodium system in n.m.r. peaks with $\delta = 1.45$ ppm was evidence of isomerisation but did not provide sufficient data to identify the products. Finlayson *et al.*[15] found that 2,2,5-trimethylhexane was the major product over sintered rhodium at 513 K and obtained evidence for a D_{11} ion ($m/e = 124$) in the relevant mass spectrum. Our results for reaction of TMP over rhodium at 393 K show small maxima for the D_8 and D_{11} ions, table 3, which may have resulted from isomerised products. Since the peaks around $\delta = 1.45$ ppm would have represented secondary or tertiary deuterium atoms in the isomerised products it is probable that primary deuterium atoms in these products contributed to the same region of the n.m.r. spectrum as the primary atoms in exchanged TMP, as suggested in table 5.

No evidence for isomerisation of DMP or TMB was found in our work over rhodium or the other three metals and it is of interest to consider why only TMP should react in this way. The results reported by Finlayson *et al.*[15] provide a possible explanation. The main type of isomerisation observed with TMP over rhodium films was the formation of 2,2,5-trimethylhexane and the mechanism was thought to involve a 1,2-neopentyl shift of an adsorbed alkyl species. This type of reaction cannot occur with the smaller molecules DMP and TMB which would have to isomerise by a 1,2-methyl shift: a reaction which occurs less readily on rhodium films than the neopentyl shift.[15]

Palladium

The results in table 1 show that the most important reaction with all three compounds over palladium was stepwise exchange. With DMP, even at 460 K, the agreement between the mass-spectrometric distribution of deutero-ions and the calculated random values is good and the amount of deuterium in $-CHD_2$ groups is close to the expected value. On the other hand, with TMP at 456 K there appears to be a small contribution either from multiple exchange or possibly even from isomerisation, *cf.* results[15] with sintered films at 468 K. Nevertheless, it is clear that the dominant mechanism with all three compounds on palladium is the reversible formation of adsorbed alkyl intermediates and that little dissociation to either $\alpha\alpha$- or $\alpha\gamma$-adsorbed species takes place. The behaviour of palladium with the hydrocarbons containing quaternary carbon atoms is in marked contrast to the very extensive multiple exchange found with other hydrocarbons[1,2] which can lose hydrogen atoms to adsorbed alkene and so form multiply exchanged products by the $\alpha\beta$-process, *i.e.* the interconversion between adsorbed alkyl and adsorbed alkene intermediates.

The kinetically well behaved exchange reactions observed with palladium, fig. 1, and the identical rates and common activation energy for all three reactants, fig. 3, may be a consequence of the fact that stepwise exchange and little else is occurring over palladium in the temperature range used. The carbon–hydrogen bond strengths in the methyl groups attached to the quaternary carbon atoms are presumably similar for all the reactants and the minor differences in the nature of the rest of the molecules have no influence on the reaction over palladium.

Rhodium

This metal gives the greatest contributions from multiple exchange with all three reactants as shown by the mass spectrometric distributions in table 3, and the n.m.r. analyses in table 5 and fig. 5 and 7. Process II, multiple exchange in a single methyl group, leading to D_2 and D_3 ions and forming the groupings $-CHD_2$ and $-CD_3$ without substantial exchange in the rest of the molecule is an important component of the reactions particularly with DMP but also with TMP and to a lesser extent TMB.

The difference between the reactants in regard to the extent and contribution of more general multiple exchange over rhodium is demonstrated most clearly in the values in fig. 4 of M which are higher for TMB than for DMP or TMP. The interest lies in the extent to which ions with 10 or more deuterium atoms are observed in the early stages of reaction with TMB or TMP. Such ions provide evidence for initial products resulting from a multiple exchange process capable of exchanging both ends of the molecules. A mechanism involving $\alpha\delta$-adsorbed intermediates is necessary to give this kind of exchange with TMB. Two mechanisms might operate with TMP, multiple exchange through $\alpha\varepsilon$-adsorbed species or propagation of the exchange over the whole molecule through $\alpha\gamma$-species involving the central $-CH_2-$ group. The latter can be ruled out since no evidence for deuterium atoms in the methylene group was found in the n.m.r. spectra of the products. Bearing in mind possible contributions from multiply exchanged isomerisation products of TMP, we do not believe that sufficient D_{10} or higher ions are observed to indicate that $\alpha\varepsilon$-diadsorbed species contribute significantly to the exchange of this molecule over rhodium. In other words, TMP and DMP show similar extents of general multiple exchange involving $\alpha\gamma$-intermediates which can lead to complete exchange of DMP and exchange limited to the three methyl groups at one end only of TMP. The situation is different with TMB which gives initially more ions in the range from D_{10} to D_{15} than from D_4 to D_9. Obviously the exchange process can propagate over all six methyl groups and this requires a mechanism involving interconversion between alkyl and $\alpha\delta$-diadsorbed intermediates which we call process IV. The maxima in the

distributions of the ions at D_9, D_{12} and D_{15} which can be seen in the results for reaction at 394 K in table 3 provide evidence of another aspect of process IV. There must be some means which helps to complete the exchange of the methyl groups involved in the $\alpha\delta$-bonding to the catalyst surface. A likely explanation of this behaviour is that $\alpha\delta$-intermediates can interconvert with $\alpha\alpha\delta$-adsorbed or more highly dissociated forms. The shape of the distributions of ions suggests that rhodium forms $\alpha\delta$-adsorbed species more readily than $\alpha\gamma$-adsorbed intermediates with TMB. The n.m.r. traces in fig. 5 and 7 show that TMB gives more of the $-CD_3$ grouping with high exchange in the remainder of the molecule than either DMP or TMP and this is confirmed by the quantitative results in table 5. All these results combine to demonstrate that with TMB over rhodium the main mechanisms of exchange are stepwise exchange together with process IV and a minor contribution from process II. On the other hand with DMP and TMP, stepwise exchange and processes II and III occur together with some isomerisation of TMP.

Self-poisoning of the exchange reactions appears to be a characteristic of rhodium catalysts and as shown in fig. 2 the influence of self-poisoning is greater with DMP and least with TMP. The explanation is probably the formation of more highly dissociated adsorbed species which are more strongly adsorbed and less readily rehydrogenated. Such species may be important for hydrogenolysis which is known[16] to occur with DMP at 463 K, *i.e.* only some 40 K above the highest temperature used in this work with rhodium. It is not surprising that the results for rhodium in fig. 3 show the greatest scatter of any of four metals from a common Arrhenius line for the three reactants because of the variety of mechanisms and possible complications at higher temperatures from self-poisoning of the exchange reactions.

Iridium

Results in tables 2 and 4 show that the dominant process with all three reactants over iridium is stepwise exchange with a minor contribution from process II, methyl-group exchange. General multiple exchange is just detectable and appears to be more extensive with TMB, see table 2 and fig. 4, than with the other reactants. So, as with rhodium, $\alpha\delta$-adsorbed species may be formed more readily than $\alpha\gamma$-species, but neither plays a substantial part in the mechanism of exchange over iridium.

Platinum

Results in table 2 and 4 and fig. 6 show that for all three reactants the mechanisms in order of importance are stepwise exchange, process II and process III. The character of process III is not the same on platinum as on rhodium. The amounts of the ions from D_4 upwards observed in reactions over platinum decrease with increasing deuterium content and the average number of deuterium atoms acquired by any molecule undergoing the $\alpha\gamma$-type of exchange over platinum is not as great as with rhodium. This implies that the number of alkyl to $\alpha\gamma$-adsorbed interconversions before an exchanged molecule desorbs is not as large on platinum as on rhodium. The M values for all three reactants are similar over platinum and the extent of multiple exchange depends mainly on the temperature and not on the nature of the hydrocarbon. The results in fig. 6 show that the n.m.r. traces for fairly extensively reacted TMB and TMP are similar and the resonances for $-CHD_2$ and $-CD_3$ groupings are broadened but not resolved into components. Clearly, the average number of γ isotopic shifts is insufficient to give rise to separate resonances as was found with rhodium. At 423 K, TMB and TMP both give *ca.* 0.8% of ions in the range from D_{10} to D_{14} at 15% conversion, see table 2, but this does not amount to significant evidence for a contribution from $\alpha\delta$- of $\alpha\varepsilon$-adsorbed intermediates since 1% of the molecule will have undergone repeated reaction at this conversion.

Relative Rates

The results in fig. 3 permit a comparison of the relative activities of the four metals fo exchange of the three hydrocarbons. The ratios of the activities at 400 K ignoring an differences in the degree of dispersion of the catalysts are 260:120:60:1 for Pt:Ir:Rh:Pd These ratios are in broad agreement with results from earlier studies[10,11] with DMP an are influenced markedly by choice of temperature because of the different activatio energies on the four metals.

The authors are grateful to Prof. J. K. A. Clarke for supplying a sample of TMP and t Prof. J. J. Rooney for stimulating our interest in these problems. We appreciate th skilful assistance of Dr I. H. Sadler who obtained the n.m.r. spectra using the S.E.R.C high-field facility at Edinburgh.

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Evidence for the Formation of an αδ-Adsorbed Hydrocarbon Intermediate on a Rhodium Catalyst†

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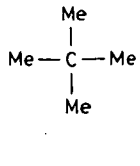
Exchange of 2,2,3,3-tetramethylbutane with deuterium over rhodium provides evidence for a mechanism involving αδ-adsorbed intermediates.

The role of αγ-absorbed intermediates in the exchange of hydrocarbons with deuterium on metal catalysts was demonstrated many years ago through studies[1] with 2,2-dimethylpropane (**1**). The main process for the exchange of this compound is stepwise exchange (**I**), involving reversible formation of adsorbed alkyl intermediates, but two other processes also contribute; these are multiple exchange limited to a single methyl group (**II**) and multiple exchange ranging

† The terms αδ- and αγ-adsorbed conform to the usual nomenclature in publications on catalysis and are equivalent to 1,4- and 1,3-adsorbed, respectively.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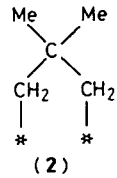
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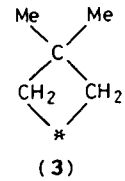
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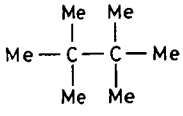
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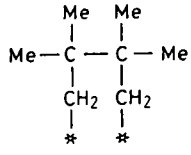
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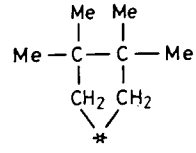
(6)

over the whole molecule (**III**). The contribution from process **III** is greater on rhodium than on other metals[1—3] and becomes more important as the temperature is increased. The mechanism of this reaction, which permits the exchange of all four methyl groups in (**1**), must involve interconversion between adsorbed alkyl and αγ-adsorbed intermediates; these may require two surface sites (**2**) or can be represented[4—6] as a metallocyclobutane (**3**) on a single site.

The purpose of the present work is to determine whether αδ-adsorbed intermediates can be formed with appropriate hydrocarbons. The compound 2,2,3,3-tetramethylbutane (**4**) is a good test reactant to settle this question and also to establish the relative importance of mechanisms involving αγ- or αδ-adsorbed intermediates. The latter, which again may involve two sites (**5**) or a metallocyclopentane (**6**) on one site, would permit the multiple exchange to range over the whole molecule. In contrast, if αγ-adsorbed intermediates are formed but αδ-species are not, the exchange process could not propagate beyond the three methyl groups attached to one of the two central carbon atoms in (**4**). Exchange of (**4**) with deuterium has been reported recently on platinum[7] and rhodium[8] catalysts but in neither case were extensively exchanged molecules observed.

The present reactions were carried out in a static system[9] connected by a capillary leak to a Vacuum Generators Micromass 601 spectrometer. The charge of hydrocarbon (693 Pa) in the reaction vessel was 3.5×10^{19} molecules with an 8 : 1 ratio of D_2 : hydrocarbon. The silica-supported rhodium catalyst,[10] containing 10^{-4} mol metal g^{-1} silica, was reduced in flowing hydrogen for 1 h at 673 K and evacuated for 30 min at the same temperature. The reaction was followed from the composition of the fragment ions $C_7X_{15}^+$ (X representing H or D) formed by loss of a methyl group from the parent molecule ionised by 35 eV electrons. The usual corrections for naturally occurring isotopes and fragmentation to other ions were made and also the peak corresponding to $C_7D_{15}^+$ was corrected for a small amount of the parent ion, $C_8H_{18}^+$, equivalent to 0.28% of the $C_7H_{15}^+$ peak. Product distributions at similar conversions at three temperatures are given in Table 1 together with a comparable result for (**1**) at the highest temperature in terms of the composition of the $C_4X_9^+$ ions. Rates and the contributions from the various exchange processes are shown in Table 2.

Several points emerge from the results, in Table 1 and at other conversions, and these are discussed in terms of four processes.

Process **I**. In every case stepwise exchange is the most important component of the overall reaction and gives the D_1-species as the main product. The rates of reaction of (**1**) and (**4**) are similar at 393K.

Table 1. Isotopic composition of the $C_7X_{15}^+$ ions from (**4**) and the $C_4X_9^+$ ions from (**1**) after 15% reaction with deuterium on rhodium.

Reactant	(4)	(4)	(4)	(1)
T/K	344	363	394	393
D_1	11.83	11.54	9.57	10.06
D_2	1.76	1.59	1.86	2.13
D_3	0.65	0.52	0.68	1.40
D_4	0.14	0.12	0.24	0.51
D_5	0.06	0.06	0.10	0.26
D_6	0.03	0.04	0.05	0.19
D_7	0.03	0.04	0.05	0.15
D_8	0.04	0.06	0.14	0.15
D_9	0.11	0.20	0.32	0.15
D_{10}	0.04	0.09	0.19	—
D_{11}	0.05	0.09	0.22	—
D_{12}	0.12	0.22	0.40	—
D_{13}	0.05	0.09	0.26	—
D_{14}	0.06	0.13	0.39	—
D_{15}	0.05	0.22	0.52	—

Table 2. Rates of reaction and contributions from the various processes for the exchange of (**4**) and (**1**).

Reactant	*T*/K	Initial rate *r*/molecule s^{-1} (mol Rh)$^{-1}$	Process contribution (%) I	II	III	IV[a]
(**4**)	344	5.3×10^{20}	85	11	—	4
(**4**)	363	1.22×10^{21}	82	9	—	9
(**4**)	394	5.1×10^{21}	69	14	—	17
(**1**)	393	8.6×10^{21}	73	21	6	—

[a] Process **IV** is the multiple exchange ranging beyond one methyl group with (**4**).

Process **II**. Methyl group exchange occurs to an appreciable extent as shown by the formation of the D_2- and D_3-ions. The values in Table 2 for the contribution of process **II** were estimated after allowing for the fraction of the D_2-ion formed by successive stepwise exchange. Process **II** occurs to a greater extent at 393K with (**1**) than with (**4**).

Process **IV**. The significant amounts of products beyond the D_9-ion with (**4**) provide clear evidence for a multiple exchange process ranging over the whole molecule with a mechanism involving αδ-absorbed intermediates. A special feature of the product distributions is the existence of maxima at the D_9-, D_{12}-, and D_{15}-ions indicating that the completion of methyl group exchange occurs more readily in association with process **IV** than in process **II**. This observation suggests that while the reacting molecules are held on the surface as αδ-intermediates interconversion can occur with species such as ααδ-adsorbed or other more highly dissociated forms related to (**5**) or (**6**).

Process **III**. The more highly exchanged products from (**1**) are evidence for a mechanism involving αγ-adsorbed intermediates. We cannot exclude a possible contribution from process **III** to the formation of the multiply-exchanged products from (**4**) but the shape of the distributions indicates that it is small compared with that of process **IV**. The conclusion is that rhodium forms αδ-adsorbed intermediates in preference to αγ-adsorbed species. This conclusion is confirmed by the small contribution of process **III** with (**1**) at 393K compared with the part played by process (**IV**) with (**4**). In estimating the percentages in Table 2 attributed to processes **III** and **IV**, the amounts of the D_4-ion from (**1**), and both the D_4- and D_5-ions from (**4**) were ignored as these products were likely to have originated through successive reactions by processes **I** and **II**.

The results with (4) give some indication of activation energies for the various processes. The value for the overall exchange reaction is 54 kJ mol^{-1}. The effects of temperature on the relative contributions of **II** to **I** and of **IV** to **I** show that the additional activation energies of processes **II** and **IV** compared with **I** are 10 and 38 kJ mol^{-1}, respectively.

The evidence that αδ-adsorbed intermediates are formed to a significant extent with (4) provides some support for the suggestion[6] of a role for metallocyclopentane intermediates in the reactions of hydrocarbons on some metals.

We are grateful to Professor Rooney for suggesting the importance of seeking evidence for αδ-adsorbed intermediates in hydrocarbon exchange reactions and to Dr. Maier for a preview of his more recent work.[8]

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4.5 CONCLUSIONS

1. Although generally of a poor dispersion the three catalaysts Pt/TiO_2, Pt/Nb_2O_5 and Rh/Nb_2O_5 exhibit SMSI characteristics.
2. The platinum supported on titania and niobia behaves in a more similar manner to alumina-supported than to silica-supported platinum after a LTR pretreatment.
3. Rhodium is a more efficient metal for hydrogenolysis than platinum.
4. There is a stronger SMSI effect with niobia as the support than anatase.
5. The hydrogenolysis of 2-methylbutane is a far more structure-sensitive reaction than n-pentane hydrogenolysis.
6. The exchange of 2-methylbutane was more susceptible to surface changes than the hydrogenolysis reaction.
7. Dehydrogenation of 2-methylbutane occurred only over HTR Pt/Nb_2O_5 and not with HTR Pt/TiO_2 or HTR Rh/Nb_2O_5. This may indicate that the active sites produced by SMSI on the former are different from those on the latter two catalysts.

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CHAPTER 5

MECHANISTIC STUDIES OF HYDROCARBON EXCHANGE REACTIONS OVER SUPPORTED METAL CATALYSTS

I Linear and Branched Alkanes

5.1 INTRODUCTION

As previously discussed the use of ^2D nmr to study in further detail the process of deuterium exchange of cyclopentane over supported metal catalysts provided clarification of the processes occurring over rhodium and nickel catalysts[1]. In this chapter the investigations carried out, using the combined techniques of mass spectrometry and ^2D nmr, on the exchange reactions of linear and branched alkanes over supported metal catalysts are reported. The principal objective of the work was to use the techniques to obtain mechanistic information on the reactions of a series of alkanes with deuterium over supported rhodium, platinum, iridium and palladium catalysts. The main body of the work concerns propane and 2-methylpropane, but butane, 2-methylbutane and n-pentane were also studied.

A further objective of the study was to deduce from the nmr spectra the incremental isotopic shifts caused by deuterium atoms separated from the observed deuteron by two (α-shift), three (β-shift) or four bonds (γ-shift). In common with deuterium isotope effects observed for other nuclei it was expected that these incremental shifts would be linearly additive[2,3] and would allow the

recognition and estimation of various groupings of deuterium atoms in the exchanged molecules.

5.2 EXPERIMENTAL

The exchange reactions were carried out on a static system linked to a mass spectrometer, i.e. line 1 as described in 3.2. The collection of the exchanged hydrocarbon for subsequent analysis by ^2D nmr has also been described in section 3.3. The preparation of the platinum and rhodium catalysts, each with 10^{-4} mol metal/g silica, has been described[4]. The pretreatment of these catalysts, as outlined in section 3.3, included reduction at 673K in flowing hydrogen for 1 hr and subsequent evacuation at 723K for 0.5 hr before cooling to reaction temperature. The two palladium catalysts were pretreated in a similar manner. These had markedly different concentrations of metal; Pd(A), from Johnson Matthey, contained 4.7×10^{-4} mol metal/g charcoal and Pd(B), from I.C.I., had 2.5×10^{-6} mol metal/g calcium aluminate. The iridium catalyst contained 2×10^{-5} mol metal/g γ-alumina and was reduced at 748K overnight for 16 hrs with evacuation at the same temperature for 1 hr[5].

Experiments in which approximately 10% reaction had taken place provided most information about the mechanisms of alkane exchange. At this stage most of the exchanged products will have been produced from only one visitation of the reactant molecule to the surface, i.e. initial

products. This was adequate for reactions where the metals encouraged multiple exchange, i.e. more than one D incorporated per product molecule, but where the exchange reaction proved to be stepwise it had to be carried further to incorporate sufficient D into the products to allow ^{2}D nmr analysis. Also to allow more accurate determination of the incremental shifts caused by the deuterium atoms, experiments with propane and 2-methylpropane were continued until the reactants had equilibrated.

The mass spectra were corrected for naturally occurring ^{13}C and for fragmentation. The factors for the latter were based on the fragmentation pattern for the alkane measured before each experiment. The ionising voltages used and typical fragmentation patterns obtained for the hydrocarbons used in the present study are given in table 5.1. It was assumed that the fragmentation factors for the perdeutero-ions were 65% of those for the light species as recommended[6] on a detailed examination of the mass spectra of equilibrated deuteropropanes. This fragmentation procedure worked satisfactorily with the exchanged alkanes and effectively eliminated the observed amounts of the fragment ions with m/e values below those of the unexchanged parent or pseudo-parent ion.

5.3 PROPANE

Mass spectrometric analyses for experiments carried

Table 5.1

Ionising Voltages and Fragmentation Factors for the Alkanes used in the Present Study

hydrocarbon	eV	No. of H atoms lost 0	1	2	3	4
C_3H_8	10	1.000	0.757	0.128	0.103	0.007
$(CH_3)_3CH$[a]	15	1.000	0.347	0.230	0.007	0.011
$n\text{-}C_4H_{10}$	20	1.000	0.200	0.051	0.052	0.007
$(CH_3)_2CHC_2H_5$	15	1.000	0.025	0.010	0.004	-
$n\text{-}C_5H_{12}$	15	1.000	0.063	0.011	0.003	-
$(CH_3)_2CHCH(CH_3)_2$	15	1.000	0.017	0.004	-	-

a the pseudo-parent ion, $(CH_3)_2CH^+$, was used with this alkane.

Table 5.2

Mass Spectrometric Analyses of Exchanged Propanes

Experiment	RHPR01	PTPR02	PTPR03	PDPR03	PDPR04	IRPR02
Catalyst	Rh	Pt	Pt	Pd(B)	Pd(A)	Ir
T/K	331	353	353	441	426	335
Deuterium Content						
D_0	91.5	93.5	89.4	92.8	77.6	72.3
D_1	0.9	2.3	3.7	0.7	3.3	23.6
D_2	0.6	0.5	0.9	0.1	0.7	3.6
D_3	0.7	0.5	0.7	0.2	1.0	0.4
D_4	0.7	0.4	0.7	0.3	1.0	0.1
D_5	1.1	0.4	0.9	0.4	1.4	0.0
D_6	1.3	0.4	0.6	0.4	2.4	0.0
D_7	1.6	0.7	1.1	1.7	5.2	0.0
D_8	1.6	1.3	2.1	3.5	7.4	0.0
M_X^a	5.2	4.0	4.2	6.5	5.7	1.2

^aM_X is the mean deuterium content of exchanged ions.

out over the four metals are reported in table 5.2 and the rates in figure 5.1. As a means of identifying some of the isotopic shifts an experiment was carried out using 2,2-dideuteropropane over platinum. Representative nmr spectra for deuterium in the methylene group (secondary deuterium) are shown in figure 5.2, and the nmr spectra of the methyl group (primary deuterium) from experiments PDPR04 and RHPR01 are shown in figure 5.3.

The resonance of highest frequency for the secondary deuterium in lightly exchanged samples occurred at δ = 1.307±0.003 p.p.m. but with the labelled reactant the corresponding peak had shifted to 1.314 p.p.m. For this sample the separation between the small peak representing molecules with a single secondary deuterium and the much larger peak due to molecules with two such atoms, figure 5.2(d), gave a value for the isotopic shift due to an alpha deuterium neighbour of -21.2 p.p.b. The spectra for the secondary deuterium atoms in the samples from experiments PDPR04, RHPR01 and PTPR02, figures 5.2(a), (b) and (c) respectively, were similar. They all gave a small peak corresponding to a secondary atom without deuterium neighbours and as expected from the mass spectrometric data in table 5.2, this peak was more obvious with the sample produced over platinum. The spectra also gave a broad unresolved peak, shifted by some -63 p.p.b., corresponding to secondary deuterium atoms in highly exchanged molecules. The failure to achieve resolution

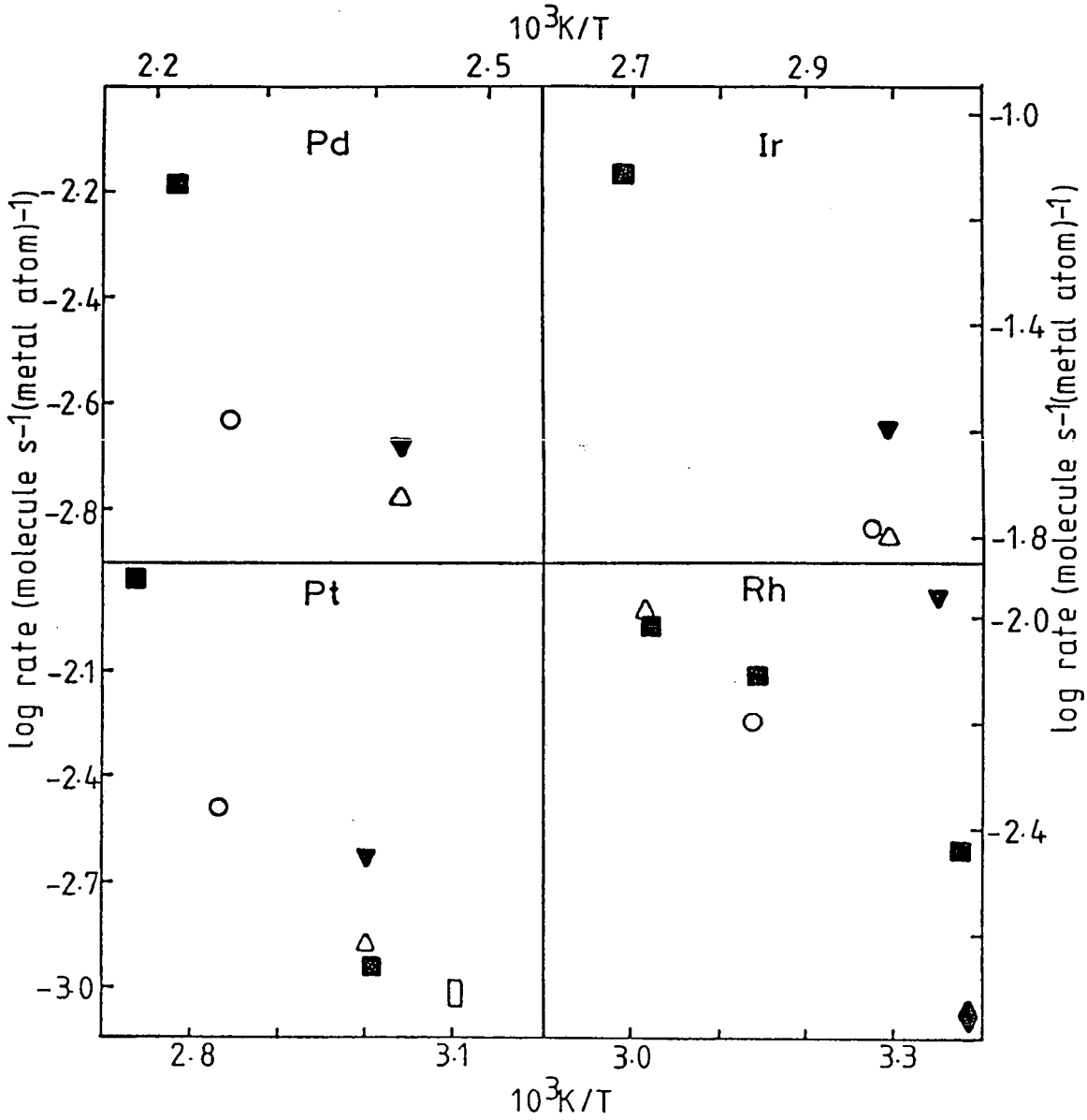

Figure 5.1 Arrhenius plots for exchange of linear and branched alkanes over supported metal catalysts:

○, propane; ■, 2-methylpropane; △, butane;

▼, 2-methylbutane, □, pentane;

◆, 2,3-dimethylbutane

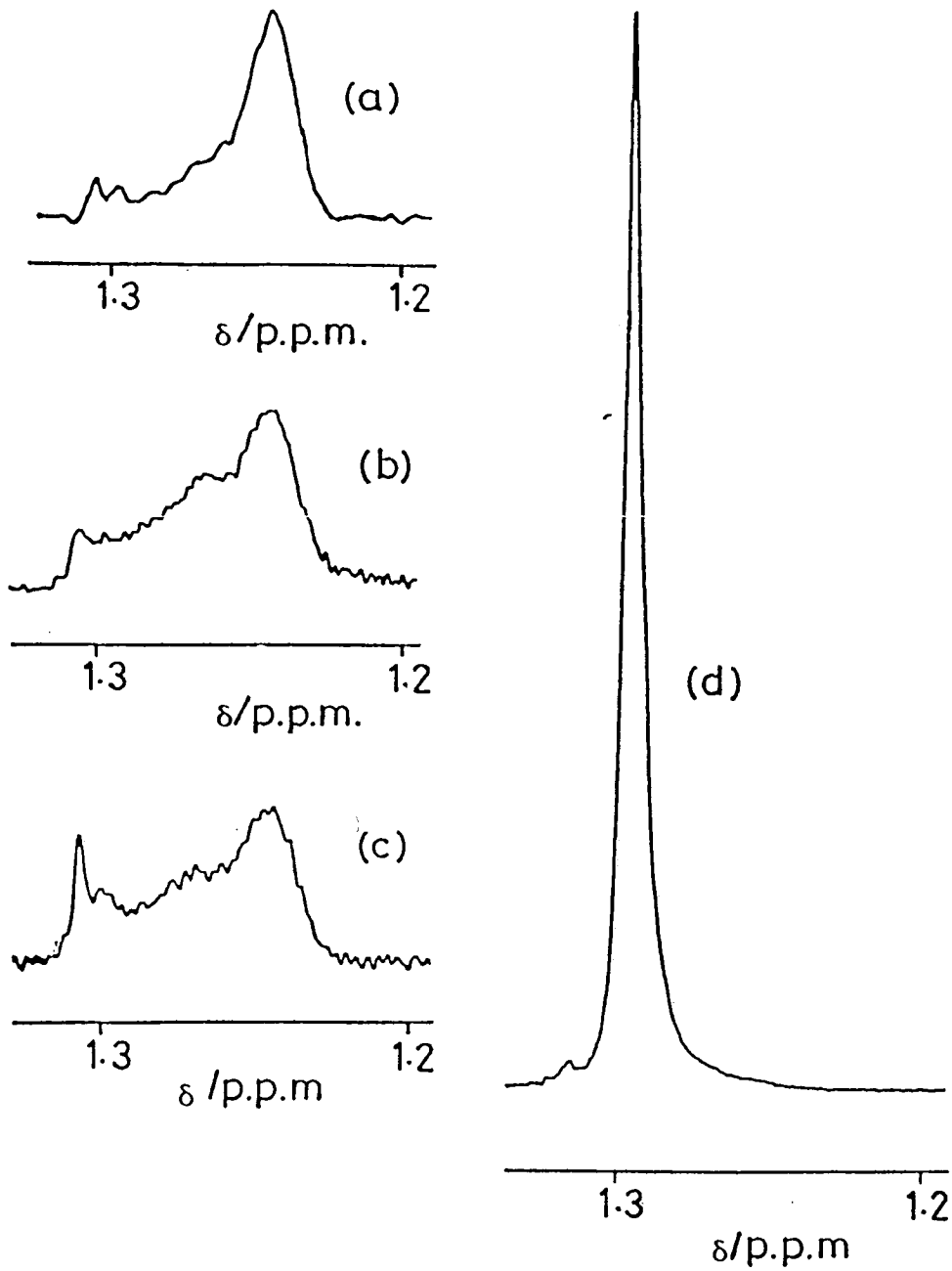

Figure 5.2 ^{2}D nmr spectra for secondary deuterium atoms in propane.

(a) C_3H_8 exchange over Palladium at 426K (PDPR04)

(b) C_3H_8 exchange over Rhodium at 331K (RHPR01)

(c) C_3H_8 exchange over Platinum at 353K (PTPR02)

(d) $CH_3CD_2CH_3$ exchange over Platinum at 413K.

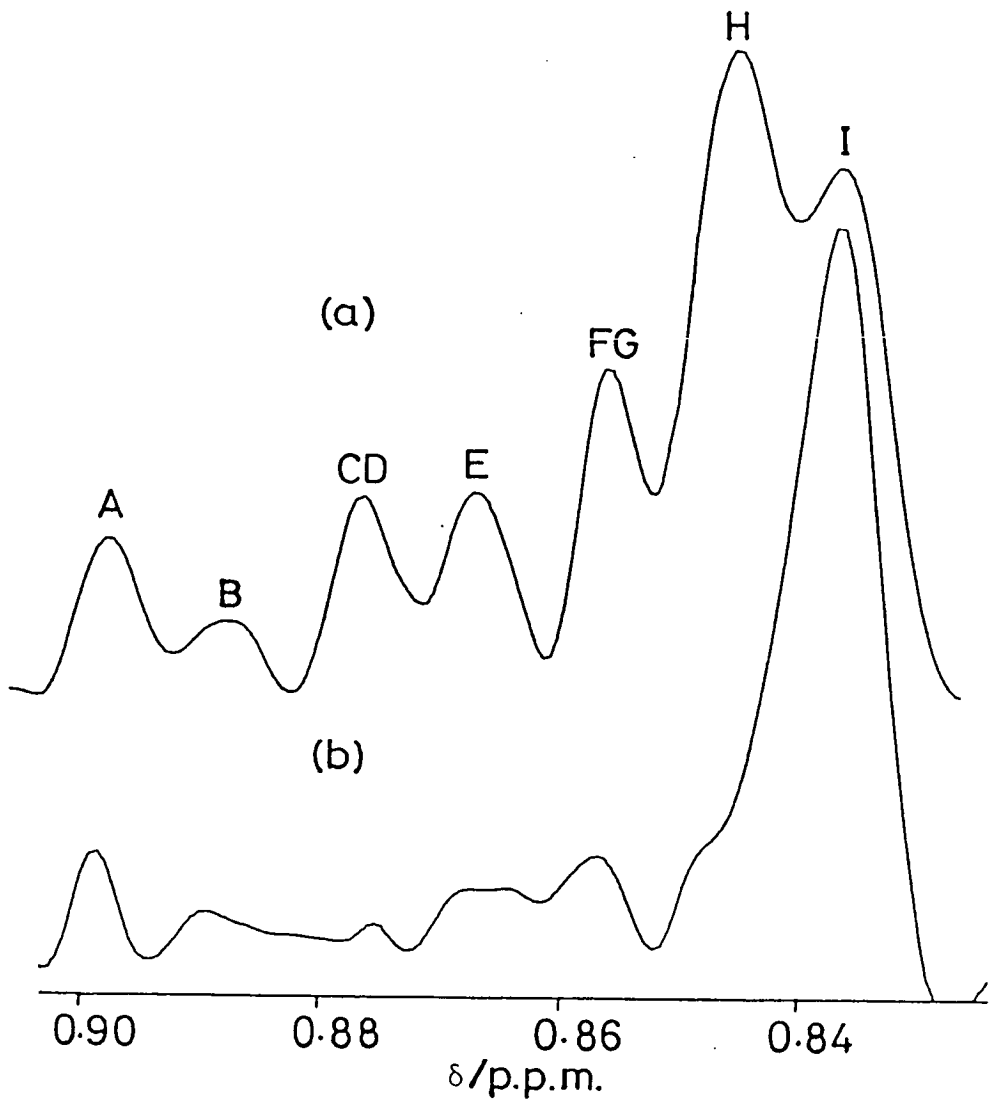

Figure 5.3 ^{2}D nmr spectra for primary deuterium atoms in propane.

(a) C_3H_8 exchange over Rhodium at 331K (RHPR01)

(b) C_3H_8 exchange over Palladium at 426K (PDPR04).

was not surprising because each secondary atom may have one alpha and up to six beta deuterium neighbours giving rise to considerable overlap from multiple deuterium-deuterium coupling. As the total shift of this broad peak was -63 p.p.b., this suggests that a beta shift must be about -8 p.p.b.

More detailed information was obtained from the region of the nmr spectra corresponding to the primary deuterium atoms. The resonance of highest frequency normally occurred at δ = 0.893±0.003 p.p.m. and this together with a series of other peaks displaced by isotopic shifts can be seen in figure 5.3(a). Each primary deuterium atom in propane may have up to two alpha and two beta neighbours and up to three gamma neighbours. Unresolved deuterium-deuterium coupling from beta neighbours causes broadening of the resonances. The sample from PTPR02, gave two clear peaks - a small one at δ = 0.8930 p.p.m. and a much larger peak at δ = 0.8313 p.p.m. On the basis of the mass spectrometric results in table 5.2 these must correspond to molecules with an isolated primary deuterium atom and to primary deuterium atoms in a perdeutero product respectively. Hence

$$2\alpha + 2\beta + 3\gamma = -61.7 \text{ p.p.b.}$$

where the Greek letters refer to the corresponding isotopic shifts. The sample from the experiment with the labelled reactant, PTPR04, gave resonances at δ = 0.8818 p.p.m. (a deuterium with two beta neighbours) and at δ =

0.8392 p.p.m. (a primary deuterium in a perdeutero molecule). Hence we have

$$2\alpha + 3\gamma = -42.6 \text{ p.p.b.}$$

From these equations and inspection of the position of the other peaks in the spectra the values selected for the isotopic shifts were α = -20.0, β = -9.5 and γ = -0.9 p.p.b. The success of these assigned values can be judged from the results given in table 5.3 in which calculated isotopic shifts are compared with observed values from experiment RHPR01. Five of the nine possible resonances - A, B, E, H, and I - could be identified as separate peaks in the nmr spectrum, figure 5.3(a), but C and D were not resolved and appeared as a single peak, as did resonances F and G. The position of each of the nine peaks will vary over a range of 2.7 p.p.b. depending on the number of gamma deuterium neighbours. The agreement between the observed position of the peaks and the calculated ranges is good and, as expected, resonances corresponding to more highly exchanged molecules tend to have greater contributions from gamma shifts.

The simplest information gained from the nmr spectra of the exchanged propanes was the relative amounts of deuterium present in the primary and secondary positions. These results are shown in table 5.4. Iridium exhibited a high preferential exchange of the primary hydrogen atoms with very little evidence of exchange occurring in the secondary positions even after 27% reaction. Both types

Table 5.3

A Comparison of the Calculated Isotopic Shifts for the Peaks in the nmr Spectra of the Primary Deuterium Atoms in Propane and the Observed Shifts for Experiment RHPR01

Resonance	Isotopic Shifts Components		$-\Delta\delta$/p.p.b.		Distribution of Primary deuterium for RHPR01
	α	β	Calc. range[a]	observed[b]	
A	0	0	0 to 2.7	-	4.7
B	0	1	9.5 to 12.2	9.9	1.5
C	0	2	19.0 to 21.7)	21.2	
D	1	0	20.0 to 22.7)		7.4
E	1	1	29.5 to 32.2	30.9	7.6
F	1	2	39.0 to 41.7)	41.9	
G	2	0	40.0 to 42.7)		13.0
H	2	1	49.5 to 52.2	52.4	41.4
I	2	2	59.0 to 61.7	61.2	24.4
					100.0

a For each selected combination of α and β shifts there may be up to three γ shifts, each of which is assumed to contribute -0.9 p.p.b.

b Results from experiment RHPR01, see figure 5.3(a).

Table 5.4

Relative Extents of Exchange per Primary, Secondary or Tertiary Hydrogen Atom in the Hydrocarbons

Metal	Pt			Rh			Pd(B)			Ir		
Hydrocarbon	1°	2°	3°	1°	2°	3°	1°	2°	3°	1°	2°	3°
Propane	0.98	1.07	-	1.07	0.80	-	1.00	1.00	-	1.33	-	-
n-Butane	0.84	1.24	-	0.96	1.07	-	0.98	1.03	-	1.61	<0.1	-
n-Pentane	0.76	1.24	-	-	-	-	-	-	-	-	-	-
2-Methylpropane	0.95	-	1.43	-	-	1.00	-	0.97	>1.10	-	<0.1	
2-Methylbutane	0.90	1.24	1.41	0.97	1.09	1.10	1.08	1.03	1.12	1.32	<0.1	<0.1
2,3-Dimethylbutane	-	-	-	0.98	-	1.10	-	-	-	-	-	-

of palladium catalyst showed similar behaviour and tended to exchange the primary and secondary hydrogen atoms to the same extent. With platinum the two positions were again exchanged to a similar extent but with evidence of the secondary hydrogen being slightly favoured. Rhodium exhibited less activity for promotion of the exchange of the hydrogens in the central carbon.

The nmr spectra of the exchanged primary groupings over platinum were similar to that shown for palladium, figure 5.3(b), except that resonance A (CH_2DCH_2-) in the former was as would be expected from the mass spectral analysis, a prominent product. This suggests that on part of the platinum metal surface alkyl desorption occurs to form a product without appreciable contributions from other reactions leading to multiple exchange. On the three metals, Pt, Pd and Rh, however there are active sites where extensive multiple exchange does occur; involving efficient interconversion between adsorbed species and leading to the formation of the perdeutero-product which shows as a clear maximum, peak I, in the spectra of platinum and palladium. Reconciliation between the mass spectral and nmr analyses for these two metals was possible. Two methods were used to extract from the mass spectrometric data calculated distributions of primary deuterium atoms in the groupings identified by nmr analysis. The methods of calculating the results will be illustrated using platinum.

The first method assumed that multiple exchange occurred by an $\alpha\beta$-process. The d_1-product was assumed to have the D atom randomly distributed between the primary and secondary positions, the d_2-product was assumed to be $CH_2DCHDCH_3$ and subsequent products were assumed to acquire D atoms in the three carbon atoms in a random fashion such that the d_3-product was assigned to CHD_2CHDCH_3, $CH_2DCD_2CH_3$, and $CH_2DCHDCH_2D$ in proportions of 2:1:3 respectively. The exchanged propanes thus generated were assigned to the identified primary groupings in the ^2D nmr spectra, as shown in table 5.5. The second method was based on an $\alpha\beta\gamma$-process (or π-allyl) for multiple exchange. The same assumptions were made about the d_1- and d_2-products, but the d_3-product was assumed to be $CH_2DCHDCH_2D$ with further products acquiring D atoms in a random fashion, as shown in table 5.6.

Both methods reproduced satisfactorily the observed distributions of products obtained over palladium and platinum, table 5.7. The percentage of the total deuterium in the secondary positions was also in good agreement. Thus either an $\alpha\beta$-process or an $\alpha\beta\gamma$-process can explain the exchange results for those two metals.

The results with rhodium are particularly interesting. There is still a mechanism which gives a small maximum for the monodeutero product but it was less pronounced than with platinum. Furthermore, the multiple exchange mechanism did not give a clear maximum in the product

Table 5.5

Propanes Generated by an $\alpha\beta$-process over Platinum and Assigned to Groupings Identified in nmr Analysis

No. of D. Atoms	%	Form	Fraction	Groupings of Primary D Atoms A	B	CD	E	FG	H	I	Secondary D Atoms
One	3.7	HHD.HH.HHH	0.75	2.78							0.93
Two	0.9	HHD.HD.HHH	1		0.9						0.9
Three	0.7	HDD.HD.HHH	0.33				0.47				0.23
		HHD.DD.HHH	0.17			0.17					0.23
		HHD.HD.HHD	0.5		0.7						0.35
Four	0.7	DDD.HD.HHH	0.07						0.14	0.05	
		HDD.DD.HHH	0.13					0.19			0.19
		HDD.HD.HHD	0.60		0.42		0.84				0.42
		HHD.DD.HHD	0.20			0.28					0.28
Five	0.9	DDD.DD.HHH	0.05							0.14	0.09
		DDD.HD.HHD	0.2		0.18				0.54		0.18
		HDD.HD.HDD	0.3				1.08				0.27
		HDD.DD.HHD	0.45			0.41		0.81			0.81
Six	0.6	DDD.DD.HHD	0.27			0.16				0.48	0.32
		DDD.HD.HDD	0.33				0.4		0.6		0.20
		HDD.DD.HDD	0.40					0.96			0.48
Seven	1.1	DDD.DD.HDD	0.83					1.83		2.75	1.83
		DDD.HD.DDD	0.17						1.1		0.18
Eight	2.1	DDD.DD.DDD	1							12.6	4.2
		Total		2.78	2.20	0.96	2.79	3.79	2.38	15.97	12.14

Table 5.6

Propanes Generated by a π-allyl-process over Platinum and Assigned to Groupings Identified in nmr Analysis

No. of D. Atoms	%	Form	Fraction	Groupings of Primary D Atoms A	B	CD	E	FG	H	I	Secondary D Atoms
One	3.7	HHD.HH.HHH	0.75	2.78							0.93
Two	0.9	HHD.HD.HHH	1		0.9						0.9
Three	0.7	HDD.HD.HHH	0				0				0
		HHD.DD.HHH	0			0					0
		HHD.HD.HHD	1		1.4						0.7
Four	0.7	DDD.HD.HHH	0.07	0						0	0
		HDD.DD.HHH	0					0			0
		HDD.HD.HHD	0.8		0.56		1.12				0.56
		HHD.DD.HHD	0.20			0.28					0.28
Five	0.9	DDD.DD.HHH	0							0	0
		DDD.HD.HHD	0.2		0.18				0.54		0.18
		HDD.HD.HDD	0.4				1.44				0.36
		HDD.DD.HHD	0.4			0.36		0.72			0.72
Six	0.6	DDD.DD.HHD	0.2			0.12				0.36	0.24
		DDD.HD.HDD	0.4				0.48		0.72		0.24
		HDD.DD.HDD	0.40					0.96			0.48
Seven	1.1	DDD.DD.HDD	0.8					1.76		2.64	1.76
		DDD.HD.DDD	0.2						1.32		0.22
Eight	2.1	DDD.DD.DDD	1							12.6	4.2
		Total		2.78	3.04	0.76	3.04	3.44	2.58	15.60	11.77

Table 5.7

Comparison of Primary Deuterium Groupings Generated by $\alpha\beta$ and π-allyl Processes with Experimental Results

Metal	Process	Percentages of Primary Deuterium A	B	CD	E	FG	H	I	Percentage Secondary Deuterium
Pt	$\alpha\beta$	8.99	7.13	3.12	9.03	12.28	7.71	51.74	28.2
							(59.45)[a]		
	π-allyl	8.88	9.73	2.43	9.73	11.01	8.26	49.94	27.4
							(58.20)[a]		
	experimental	10.80	7.60	3.40	11.20	9.30	(57.70)[a]		26.8
Pd(A)	$\alpha\beta$	2.63	2.74	1.95	5.46	14.89	9.17	63.17	26.8
	π-allyl	2.60	3.98	1.52	6.06	13.98	10.48	61.38	26.2
	experimental	3.70	3.10	2.20	7.70	12.10	(71.20)[a]		2.50
Rh	$\alpha\beta$	2.12	6.11	3.90	10.99	18.64	11.64	46.59	28.3
	π-allyl	2.09	8.62	3.04	12.16	17.12	12.84	44.11	27.2
	experimental	4.70	1.50	7.40	7.60	13.00	41.40	24.40	20.0

[a] H+I

distribution for the perdeutero-product as was the case for platinum and palladium, table 5.2. The nmr spectrum, figure 5.3(a), showed that a very substantial fraction of the primary deuterium atoms appeared as peak H, i.e. in the form CD_3CHD- with only a single deuterium atom in the secondary position. The poor correlation between the primary groupings and mass spectrum analysis, table 5.7, also indicated that exchange was not occurring by an $\alpha\beta$- or $\alpha\beta\gamma$-process. Therefore to account for these experimental results another mechanism must be considered. The differences can be understood if it is assumed that some multiple exchange occurs by the $\alpha\gamma$-process, i.e. interconversion between adsorbed n-propyl radicals and 1,3-diadsorbed species. In order to demonstrate this, consider four of the resonances, A, B, H and I, but it must be noted that 80% of the average of 0.433 deuterium atoms per propane molecule, i.e. 0.354, will be in the primary position and the remaining 20% will be in the secondary position.

In resonance A the nmr spectrum shows that 4.7% of the primary deuterium appeared as CH_2DCH_2-. The maximum amount that could arise from the 0.9% of the d_1-compound is 0.9/0.354 = 2.5%. Thus resonance A must include contributions from the d_2- and d_3-compounds, some of which have to be of the type $CH_2DCH_2CH_2D$ and $CH_2DCH_2CHD_2$, i.e. without a secondary deuterium atom. Therefore there must be a contribution over rhodium from a multiple exchange

process for propane involving the reversible formation of an $\alpha\gamma$-intermediate.

The nmr spectrum showed that only 1.5% of primary deuterium appeared as CH_2DCHD-, i.e. resonance B, but as table 5.7 indicates an $\alpha\beta$-process would require 6.1% of the primary deuteriums to appear in this grouping, therefore once again the conclusion is that an $\alpha\gamma$-mechanism must be involved.

A minimum of 24.4% of all the primary deuterium atoms was contained in resonance I, CD_3CD_2-. This value would be a minimum because some of the contribution from this type of grouping would have been broadened by deuterium-deuterium coupling and appeared under the H resonance. The amount of the d_8-compound is sufficient to account for all of the resonance since 6 x 1.6/0.354 = 27%. There must be little contribution, if any, from the d_7-compound to resonance I and the d_7-compound must be largely CD_3CHDCD_3, i.e. there must be a tendency not to exchange the second secondary hydrogen atom in the multiple exchange process over rhodium.

The most prominent peak in the nmr spectrum was resonance H and analysis of the spectrum showed that a maximum of 41.4% of the primary deuterium was present as CD_3CHD-. To account for this large percentage it is necessary to assume that all the d_7-compound was CD_3CHDCD_3, that all the d_6-compound was $CD_3CHDCHD_2$ and that the d_5-compound contained some CD_3CHDCH_2D. The

maximum possible contributions to resonance H from the d_7- and d_8-products are (6 x 1.6)/0.354 = 27% and (3 x 1.3)/ 0.354 = 11% respectively, i.e. a total of 38%. This is again substantial proof that over rhodium there is a mechanistic difficulty in exchanging the second hydrogen atom in the propane methylene group, which would occur if part of the multiple exchange mechanism was by an $\alpha\gamma$-process.

5.4 2-METHYLPROPANE

The mass spectrometric analyses of the fragment ions, $C_3X_7^+$, formed from the isotopic 2-methylpropanes produced over the four supported metals are reported in table 5.8 and their rates shown in figure 5.1. Representative nmr spectra for deuterium in the methine group (tertiary position) are given in figure 5.4 and for the primary deuterium atoms in figures 5.5 and 5.6.

The highest frequency for the tertiary deuterium occurred at δ = 1.689±0.002 p.p.m. As this position may have up to nine beta deuterium neighbours the signal from a multiply exchanged sample is broadened and resolution is not possible. The spectra from experiments PT2MP2 and RH2MP5E, figures 5.4(b) and 5.4(c) respectively, suggested a value for each beta shift of -7 p.p.b. Using this value it was possible to interpret the shape of the broad spectrum shown in figure 5.4(a) for the sample from experiment RH2MP3. The mass spectrometric data for this

Table 5.8

Representative Mass Spectrometric Analyses for the Reaction of 2-Methylpropane Expressed as Composition of $C_3X_7^+$ Ions

Experiment	RH2MP3	PT2MP2	PD2MP1	IR2MP2	RH2MP5E	Calc[a]
Catalyst	Rh	Pt	Pd(B)	Ir	Rh	
T/K	296	365	426	372	373	
Deuterium Content						
D_0	90.80	70.4	92.76	71.96	21.5	21.7
D_1	1.18	7.2	1.10	22.50	39.3	37.1
D_2	0.61	2.6	0.11	4.36	23.6	27.1
D_3	0.55	1.8	0.09	0.68	12.2	11.0
D_4	0.72	2.1	0.16	0.15	2.9	2.7
D_5	1.23	3.5	0.69	0.11	0.4	0.4
D_6	1.67	5.0	0.96	0.10	0.05	0.03
D_7	3.24	7.4	4.13	0.14	-	-
M_X	5.43	4.24	5.57	1.28	1.37	-

a Calculated for an average of 1.37 deuterium atoms in the $C_3X_7^+$ ions for comparison with the results from experiment RH2MP5E.

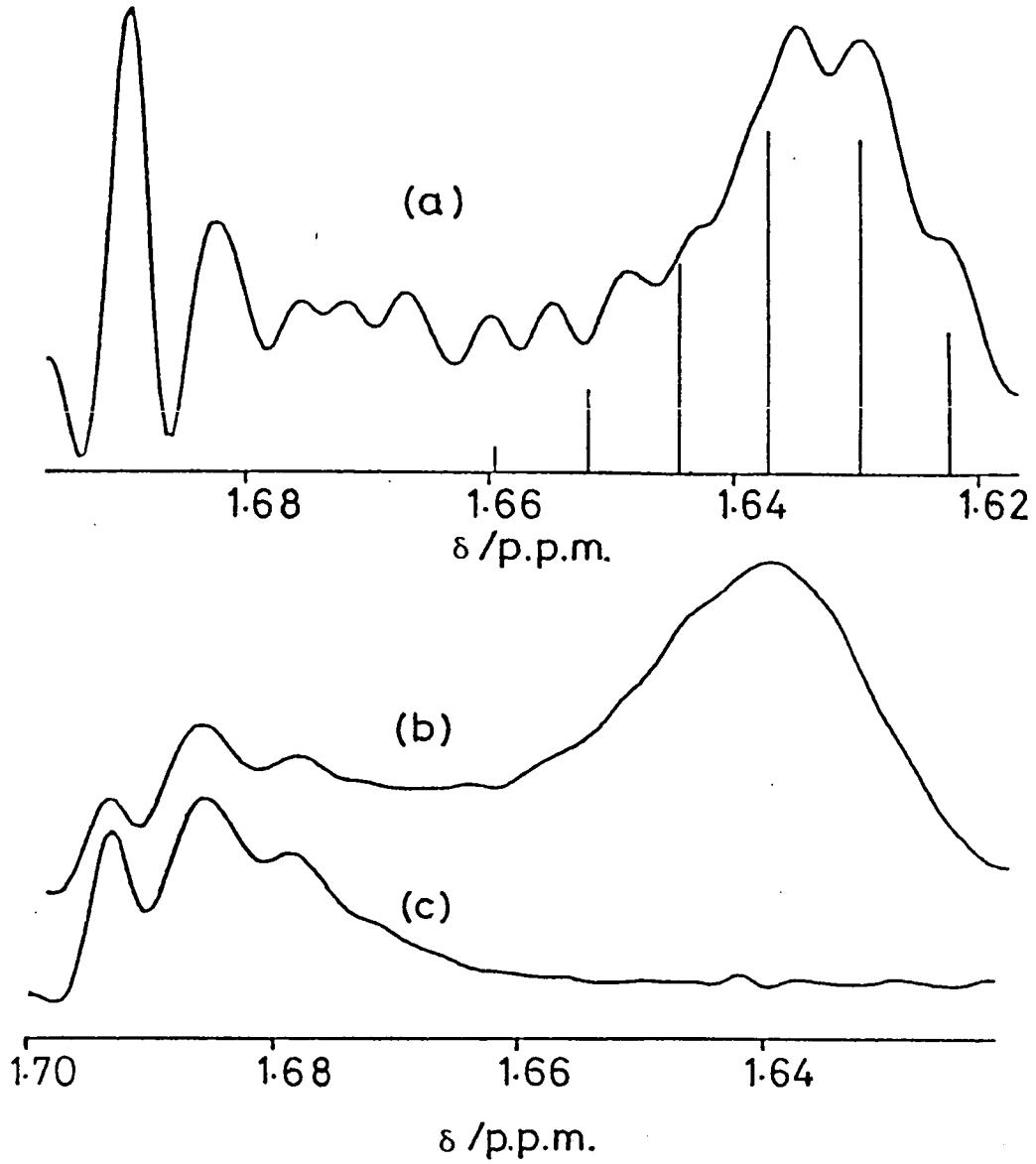

Figure 5.4 ^{2}D nmr spectra of deuterium in the methine position of 2-methylpropane.

(a) from experiment RH2MP3. The bar chart assumes a random distribution of 7.14 deuterium atoms in the methyl groups and a beta shift of - 7.6 p.p.b.

(b) from experiment PT2MP2.

(c) from experiment RH2MP5E.

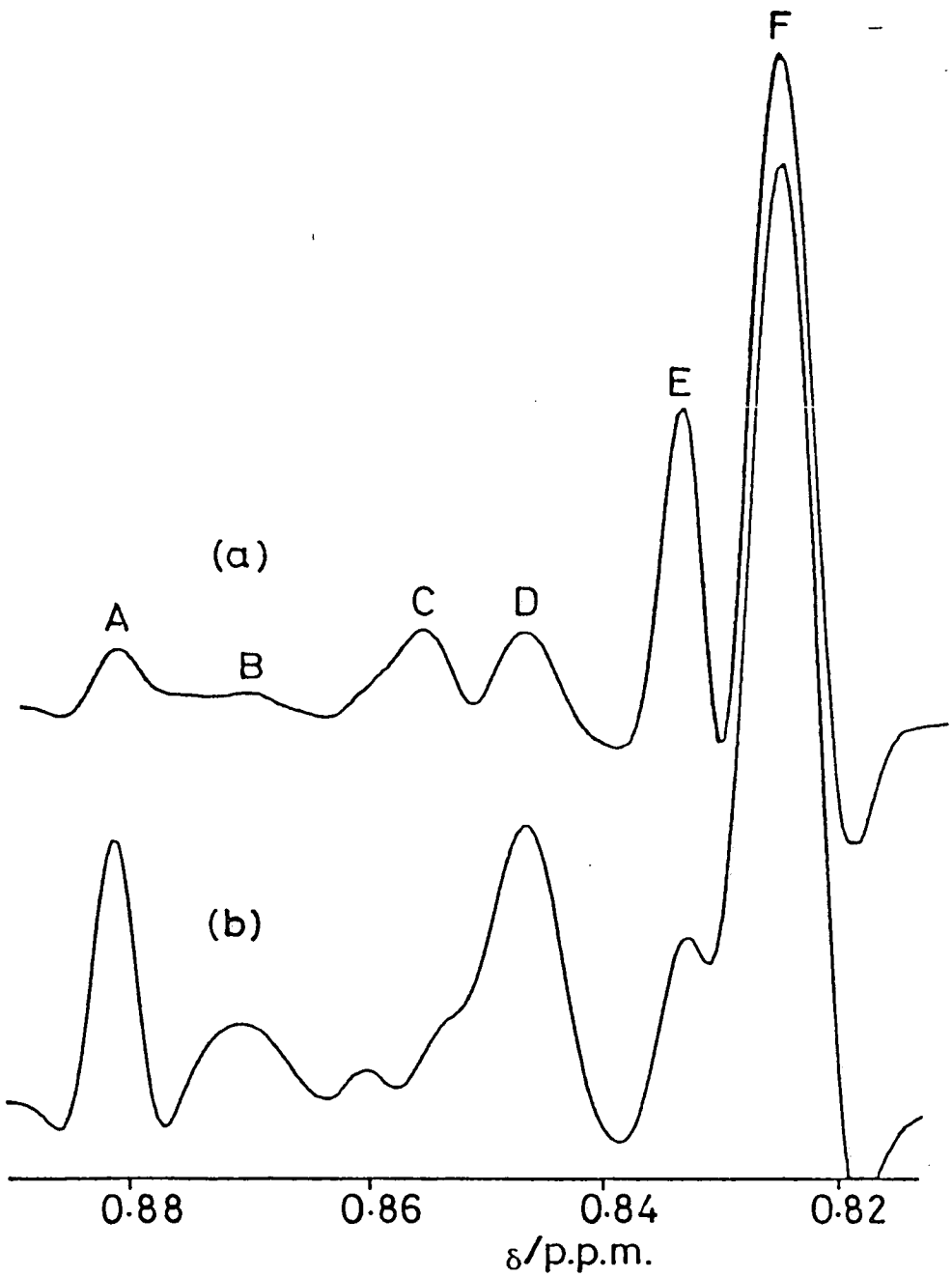

Figure 5.5 ^{2}D nmr spectra for primary deuterium atoms in 2-methylpropane.

(a) $(CH_3)_3CH$ exchange over Platinum at 365K (PT2MP2).

(b) $(CH_3)_3CH$ exchange over Rhodium at 296K (RH2MP3).

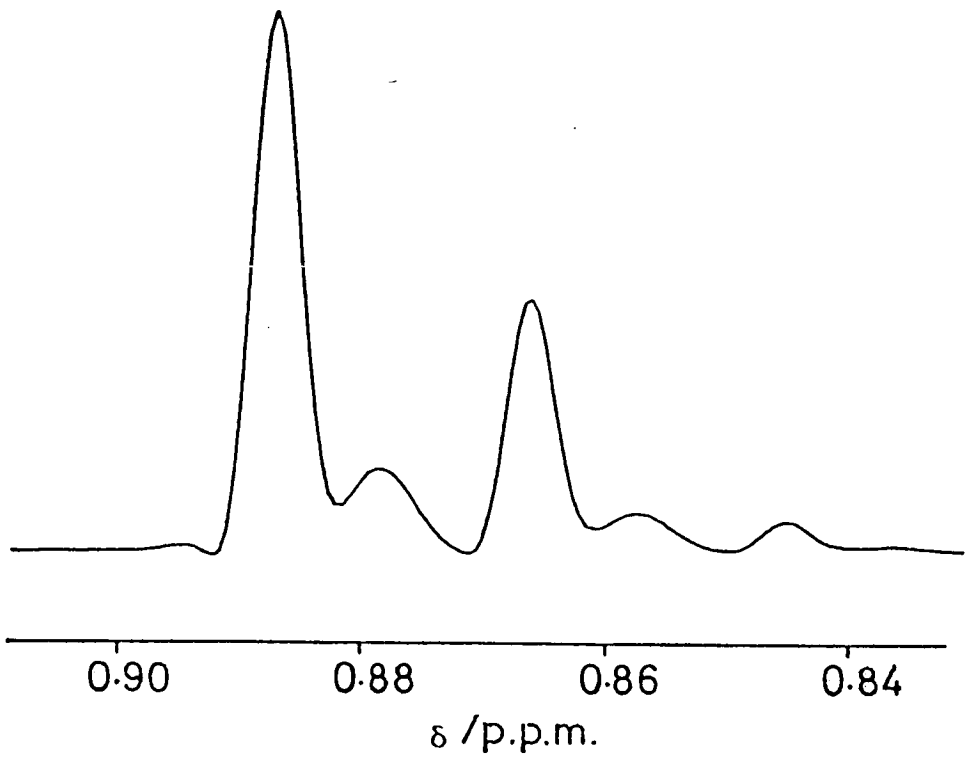

Figure 5.6 ^{2}D nmr spectrum for the primary deuterium atoms in the sample from experiment RH2MP5E.

experiment indicated that the multiply-exchanged $C_3X_7^+$ ions, i.e. ignoring the $C_3H_6D^+$ ion, contained an average of 5.55 deuterium atoms - equivalent to an average chance, d = 0.793, for a deuterium in each of the seven positions. The bar chart included in figure 5.4(a) represents the relative contributions to be expected for a random distribution of 9 x 0.793 = 7.14 deuterium atoms in the three methyl groups with the position of the bars located on the assumption that each beta atom contributed an isotopic shift of -7.6 p.p.b. There is a general similarity between the observed spectrum and the bar chart, although of course no allowance is made for the natural width of the peaks or for further broadening due to deuterium-deuterium coupling.

The highest frequency for the primary deuterium occurred at δ = 0.886±0.003 p.p.m. and the analysis of the nmr spectra for such atoms was facilitated by the results shown in figure 5.6 for the equilibrated sample from experiment RH2MP5E. Each primary deuterium atom in 2-methylpropane can have up to two alpha, one beta and six gamma neighbours. Since unresolved coupling was limited to the one possible deuterium neighbour in the beta position, the line broadening was not sufficient to interfere with the analysis. The results from experiment RH2MP5E in figure 5.6 and table 5.9 confirm that the main isotopic shifts are α = -20.9 p.p.b. and β = -8.5 p.p.b. It is not necessary to consider the influence of gamma

Table 5.9

Resonances for Primary Deuterium Atoms in the nmr Spectrum for the Products from Experiment RH2MP5E with Isotopic Shifts and the Relative Sizes of the Peaks

Resonance	Components		$-\Delta\delta$/p.p.b.		Distribution of Deuterium	
	α	β	Calc.	Obs.	Calc.[a]	Obs.
A(CH_2DCH-)	0	0	0	0	56.4	55.2
B(CH_2DCD-)	0	1	8.5	8.6	11.9	10.7
C(CHD_2CH-)	1	0	20.9	20.9	23.7	25.6
D(CHD_2CD-)	1	1	29.4	29.4	5.0	5.2
E(CD_3)CH-)	2	0	41.8	41.7	3.0	3.3
F(CD_3CD-)	2	1	50.3			

[a] Calculated on the assumption that the chance of having a deuterium atom in any position was 0.174.

shifts as they will affect all the resonances in this sample to the same extent. Thus a satisfactory interpretation can be obtained for the distribution of the deuterium atoms in the primary groupings shown in figure 5.6 and recorded in table 5.9. The last two columns of this table show the agreement between the various resonances and the calculated values based on a mean value of d = 0.174. This latter value, d, which is the chance of having a deuterium atom in a given position was obtained from the ^2D nmr spectrum by three independent means:

(i) The ratio B/(A+B) = 0.163 gave the chance of having a **D** in the tertiary position.

(ii) Similarly, the ratio C/(C+D) = 0.170 gave another value for the same quantity.

(iii) A further value of d = 0.189 was derived from the relative amounts of deuterium in $-CH_2D$ groups (A+B) and $-CHD_2$ groups (C+D) such that $3h^2d/6hd^2$ where the chance of finding a deuterium in any position, i.e. $d = M_X/7$ and $h = 1-d$ is the corresponding chance of having a hydrogen atom.

From the mass spectrometric analysis of the $C_3X_7^+$ ions for experiment RH2MP5E an average value of 1.37D atoms per ion is obtained. This gives a further value of d = 1.37/7 = 0.196 which is essentially the same as the results gained from the nmr spectrum.

An indication of the value of the gamma isotopic

shifts on the position of the resonances for the primary deuterium atoms was obtained from nmr spectra of some additional rhodium and platinum experiments. Most of the resonances from A and C to F were observed in the spectra but the positions C to F were shifted to lower frequencies due to the influence of the deuterium atoms in gamma positions. The data are brought together in table 5.10 and show that there was a consistent additional shift of each of the resonances of about -5 p.p.b. attributable to the presence of gamma deuterium atoms. Analysis of the mass spectrometric data for the multiply-exchanged ions from the kinetic experiments indicated that the average number of gamma deuterium atoms was 4.7 in the six possible positions and this together with the mean shift of -5.5 p.p.b. suggests that the γ-shift per atom is about -1.2 p.p.b.

The main evidence about mechanisms comes from the distribution of the primary deuterium atoms in the various resonances from the results of the experiments shown in table 5.8. If the $\alpha\beta$-process was the sole mechanism for multiple exchange the initial products should not include species such as CHD_2CH- or CD_3CH- as all multiply-exchanged species should have a tertiary deuterium atom. These species, corresponding to resonances C and E, were formed to appreciable extents over the rhodium catalyst, experiment RH2MP3, showing that, as with propane, there must be substantial

Table 5.10

Isotopic Shifts for the Resonances for Primary Deuterium Atoms in the nmr Spectra from Kinetic Experiments with 2-methylpropane

Resonance	Calc. for α & β D Atoms	Isotopic Shifts ($-\Delta\delta$/p.p.b.) Observed	Mean Observed	Difference[a] between mean obs. and calc.
C	20.9	26.7, 25.9, 25.5	26.0	5.1
D	29.4	34.9, 34.7, 34.5, 34.3	34.6	5.2
E	41.8	47.8, 48.4, 47.8, 46.7	47.7	5.9
F	50.3	56.1, 56.2, 55.9, 55.6	56.0	5.7

a Attributable to the shifts due to γ deuterium atoms.

contribution from either $\alpha\alpha$- or $\alpha\gamma$- multiple exchange mechanisms over this metal. As there was no evidence from the mass spectral data, table 5.8, of any maximum or cut off in the product distribution for rhodium at the d_3-product, it is considered that, under the present experimental conditions, the $\alpha\gamma$-process is more important than the $\alpha\alpha$-process. The results for the distribution formed over platinum and palladium are more consistent with those expected for an $\alpha\beta$-process and although there is evidence for the presence of CD_3CH- in the ^2D nmr spectra this can be accounted for when the results are considered more quantitatively.

As previously mentioned in the initial stages of the reaction the grouping CD_3CH- should not be formed if the exchange is proceeding via an $\alpha\beta$- or $\alpha\beta\gamma$-process as these two mechanisms would involve replacement of the tertiary hydrogen atom. As the extent of exchange increases however the deuterium will become diluted with HD and consequently the mean chance of acquiring an H atom instead of a D atom will also increase. The mean chance of acquiring an H atom (h) at one position due to isotopic dilution can be estimated from the initial and final composition of the reacting gases:

$$\text{i.e. mean } h = \frac{0.10}{7} * \frac{\text{initial amount of D atoms}}{\text{total amount of D + H atoms}}$$

Figure 5.7 shows that the results for platinum and palladium are close to the line for a plot of the

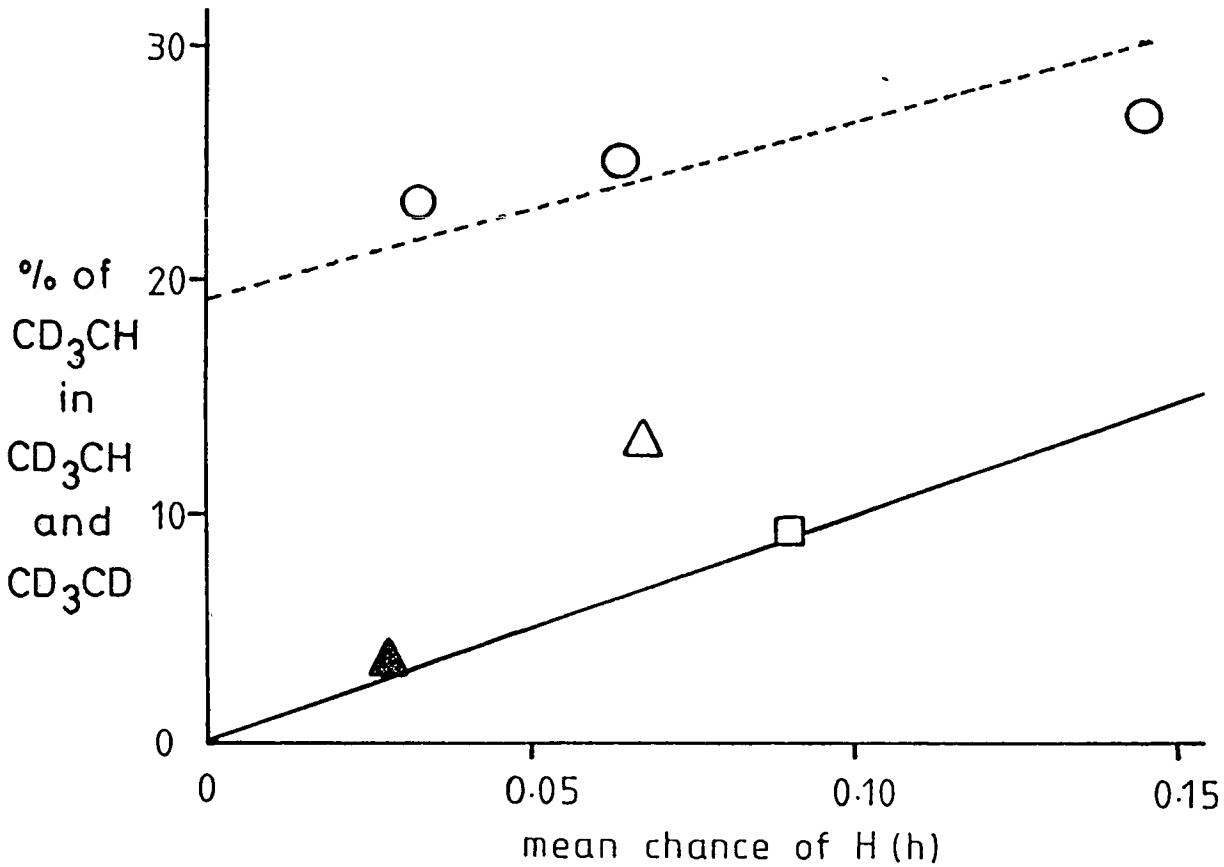

Figure 5.7 Percentage of CD_3CH- related to the mean chance of acquiring an H atom during 2-methylpropane exchange:

□Pt(365K), △Pd(A)(426K),

▲Pd(B)(426K), ○Rh(296, 319 and 332K);

the full line represents results expected for an αβ-process, and the dashed line is that expected for a 19% contribution from an αγ- (or γγ-) process.

percentage of CD_3CH- in CD_3CX-(X being H or D) versus mean h, whereas those for rhodium are well above. Thus the grouping CD_3CH- found in the nmr spectra for the results from palladium and platinum is the amount expected for an $\alpha\beta$-process due to isotopic dilution of the reacting deuterium gas with hydrogen, but the multiple exchange over rhodium must involve a contribution, of about 20%, from an $\alpha\gamma$-process.

5.5 BUTANE

The mass spectrometric analyses of butane exchanged over the four metals are presented in table 5.11 and their rates reported in figure 5.1. Representative nmr spectra of deuterium in the secondary positions are given in figure 5.8 and spectra of the primary deuterium atoms in the methyl groups are shown in figure 5.9.

The highest frequency for the secondary deuterium atom occurred at δ = 1.270±0.001 p.p.m. and as the result from experiment PDBUT1 shows, figure 5.8(a), where extensive multiple exchange occurs, the maximum of one alpha and five beta interactions which this position can be subjected to results in a broad resonance and resolution is not possible. The results from the rhodium and platinum catalysts have more d_1-product present and are less heavily exchanged so the methylene spectra from experiments RHBUT1 and PTBUT1 figures 5.8(b) and 5.8(c) respectively can be resolved to some extent. The next

Table 5.11

Mass Spectrometric Analyses of Exchanged Butanes

Experiment	RHBUT1	PTBUT1	PDBUT1	IRBUT1
Catalyst	Rh	Pt	Pd(B)	Ir
T/K	332	332	452	334
No. of D Atoms	Percentages of Products			
D_0	92.60	91.25	84.24	79.35
D_1	0.85	3.09	1.02	17.60
D_2	0.55	0.96	0.16	2.55
D_3	0.40	0.70	0.14	0.29
D_4	0.38	0.65	0.07	0.07
D_5	0.36	0.60	0.32	0.04
D_6	0.33	0.49	0.52	0.04
D_7	0.43	0.45	1.27	0.02
D_8	0.61	0.39	2.56	0.01
D_9	1.20	0.50	4.72	0.01
D_{10}	2.29	0.92	4.98	0.02
M_X	6.76	4.07	8.15	1.20

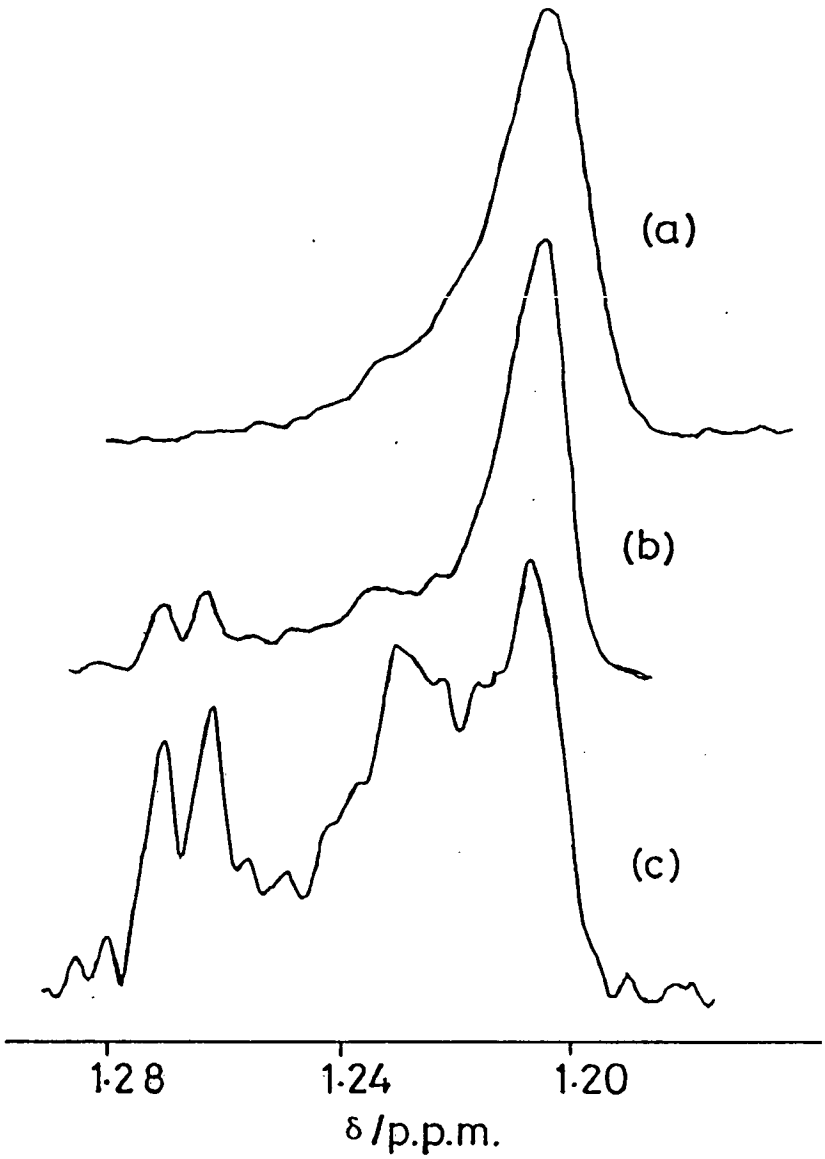

Figure 5.8 ^{2}D nmr spectra for the secondary deuterium atoms in products from butane exchange.

(a) C_4H_{10} exchange over Palladium at 413K (PDBUT1)

(b) C_4H_{10} exchange over Rhodium at 332K (RHBUT1)

(c) C_4H_{10} exchange over Platinum at 332K (PTBUT1).

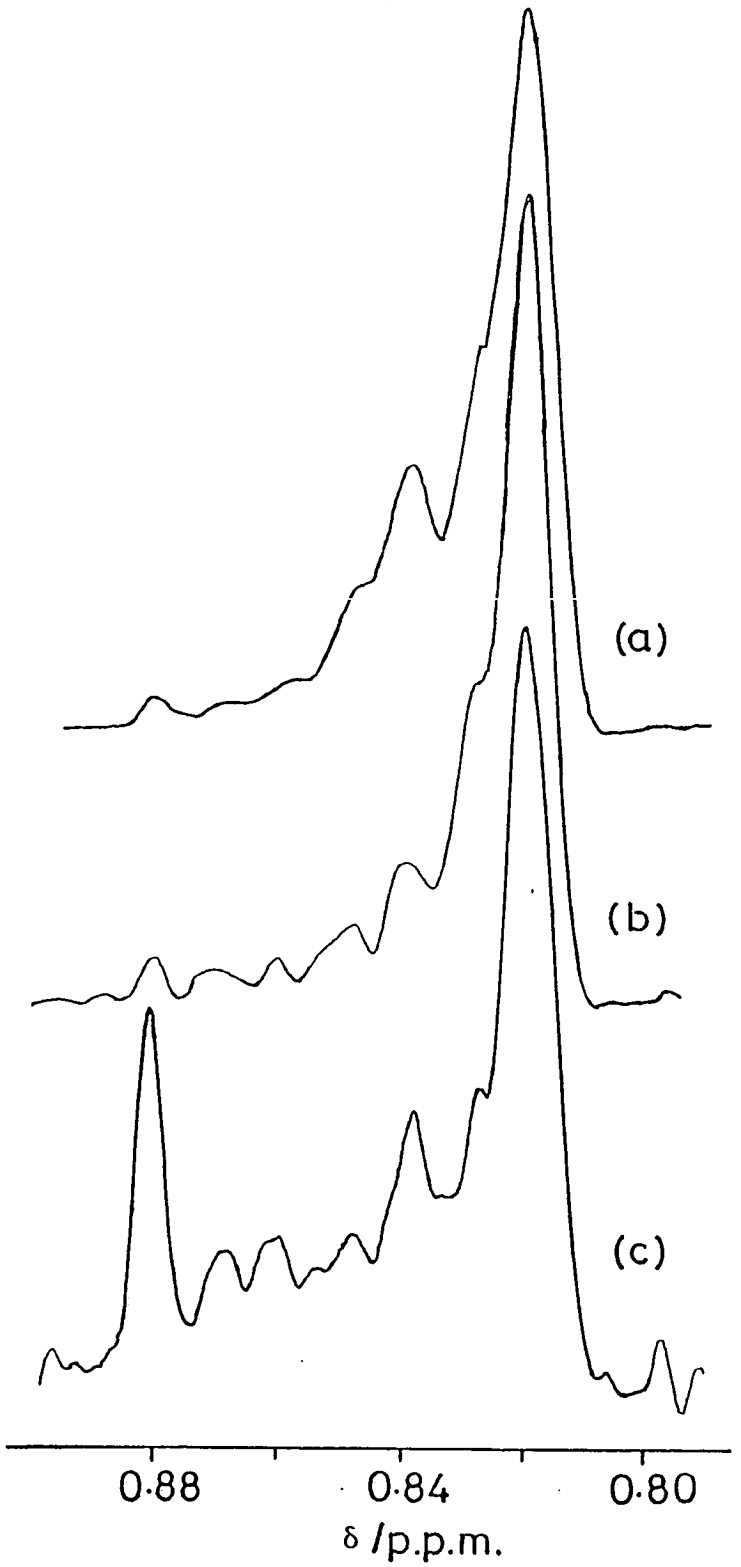

Figure 5.9 ^{2}D nmr spectra for primary deuterium atoms in products from butane exchange.

(a) C_4H_{10} exchange over Palladium at 413K (PDBUT1)

(b) C_4H_{10} exchange over Rhodium at 332K (RHBUT1)

(c) C_4H_{10} exchange over Platinum at 332K (PTBUT1).

peak appears at -7.4±0.1 p.p.b. downfield which is a typical value for a beta interaction but it is less than the -8.0 p.p.b. value found for propane. Indeed it is more akin to the -7.0 p.p.b. shift found for a *cis* beta neighbour in cyclopentane[7], and it is suggested that this grouping is $CH_3CH\ DCH\ DCH_3$ and not $CH_2DCHDCH_2CH_3$. Further assignment of other groupings apart from the fully deuterated species was not possible, therefore only three groupings of deuterium in the secondary position could be identified and quantified, the values of which are given in table 5.12.

The highest frequency for the primary deuterium occurred at δ = 0.881±0.003 p.p.m. and each primary deuterium atom in butane can be influenced by up to two alpha, two beta and two gamma deuterium neighbours. The resolved peaks from experiments RHBUT1 and PTBUT1, figures 5.9(b) and 5.9(c) respectively, could be interpreted by assuming that the alpha and beta interactions were the same as for propane, i.e. -20.0 p.p.b. and -9.5 p.p.b. respectively. The groupings thus identified and the calculated amounts of each are shown in table 5.12.

Complete reconciliation of the nmr spectra and mass spectral analyses was not possible but some qualitative observations can be made. As previously shown for propane and 2-methylpropane, iridium preferred to exchange the primary hydrogens of the n-butane with only a small amount of evidence for more multiple exchange, table 5.4. As

Table 5.12

^{2}D nmr Analysis of Exchanged Butanes

Experiment	RHBUT1	PTBUT1	PDBUT1	IRBUT1
Catalyst	Rh	Pt	Pd(B)	Ir
T/K	332	332	452	334
Primary Grouping				
CH_2DCH_2-	0.9	6.6		86.1
CH_2DCHD-	1.0	2.8		
CH_2DCD_2-	1.0	2.9	13.1	10.3
CHD_2CH_2-				
CHD_2CHD-	3.2	4.0		
CHD_2CD_2-	5.2	7.1	17.1	
CD_3CH_2-				
CD_3CHD-	46.0	4.5	69.7	
CD_3CD_2-		21.5		
Total Primary D	57.3	49.4	58.8	96.4
Secondary Grouping				
CH_3CHDCH_2-	1.4	4.1	-	3.4
$CH_3CHDCHD$-	2.2	5.2	-	
$CD_3CD_2CD_3$-	29.5	19.9	-	-
Total Secondary D	42.7	50.7	41.2	3.4

expected palladium exchanged both positions equally; producing the smallest amount of d_1-product and the greatest extent of multiple exchange. This is reflected in the nmr spectrum with a large peak corresponding to extensively exchanged butanes in both the secondary and primary positions, figures 5.8(a) and 5.9(a) respectively. A more complete analysis of the rhodium and platinum nmr spectra, table 5.12, suggests a spread of exchanged butanes. Both positions of the molecule are exchanged to a similar extent over rhodium and the spectra are similar to those of palladium, a consequence of extensive multiple exchange. Platinum also exhibited some multiple exchange with a maximum at the d_{10}-product, table 5.11, although as with the other alkanes a substantial amount of d_1-species was also produced from reversible adsorption of an alkyl intermediate. The secondary positions of the butane were more favourably exchanged, table 5.4, and the nmr results also showed that 10% of the secondary D had only one beta neighbour, table 5.12. This may have resulted from reversible adsorption of alkene associated with the internal carbons, C_2-C_3, rather than C_1-C_2.

5.6 2-METHYLBUTANE, n-PENTANE AND 2,3-DIMETHYLBUTANE

The details of the experiments using 2-methylbutane, n-pentane and 2,3-dimethylbutane as well as the mass spectrometric analyses of the final compositions of the hydrocarbons examined by ^2D nmr are given in table 5.13

Table 5.13

Mass Spectrometric Analyses of Products from the Reactions of 2-Methylbutane (2MB), n-Pentane (PEN) and 2,3-Dimethylbutane (DMB) over the Supported Metal Catalysts

Expt.	RH2MB1	RHDMB1	PT2MB1	PTPEN1	PD2MB1	IR2MB1
Catalyst	Rh	Rh	Pt	Pt	Pd(B)	Ir
T/K	299	295	333	322	411	334
Deuterium Content						
D_0	90.48	94.59	87.96	95.99	93.25	67.80
D_1	0.61	0.68	4.93	1.30	0.73	23.94
D_2	0.50	0.43	1.38	0.50	0.17	6.65
D_3	0.35	0.29	0.79	0.34	0.09	1.35
D_4	0.31	0.28	0.61	0.29	0.09	0.20
D_5	0.25	0.16	0.49	0.25	0.08	0.06
D_6	0.25	0.14	0.42	0.27	0.10	-
D_7	0.31	0.16	0.38	0.22	0.12	-
D_8	0.44	0.14	0.39	0.15	0.17	-
D_9	0.75	0.11	0.47	0.16	0.33	-
D_{10}	1.19	0.14	0.47	0.13	0.71	-
D_{11}	2.00	0.21	0.63	0.13	1.32	-
D_{12}	2.56	0.42	1.08	0.27	2.84	-
D_{13}		0.60	-	-		-
D_{14}		1.65	-	-		-
M_X	8.79	8.88	4.32	4.36	9.4	1.31

and the rates shown in figure 5.1. The relative extents of exchange in the various positions of these alkanes are given in table 5.4.

From a ^1H nmr spectrum of 2-methylbutane the expected values for a deuterium atom in the secondary and tertiary positions were δ = 1.176 p.p.m. and 1.425 p.p.m. respectively. As both atoms could be influenced by multiple-multiple deuterium coupling in a highly exchanged sample the spectra of deuterium in these positions proved to be diffuse and broad so that detailed analysis was, as with previous alkanes, difficult. The proton spectrum also indicated that the primary hydrogens attached to the C_4 carbon atom resonated at a higher chemical shift than the primary hydrogens of the methyl groups bonded to the C_2 carbon, presumably because of their slightly different environment. As the difference was only 4 p.p.b. the spectra for the primary hydrogens were rather complex which made analysis of each type of methyl group impractical. Thus the only quantitative data which could be deduced from the nmr spectra were the relative amounts of deuterium in each of the three positions of this molecule, given in table 5.4.

The positions of the various resonances expected from n-pentane were acquired from a proton nmr spectrum. This indicated that the central methylene group resonance was at δ = 1.229 p.p.m. with the C_2 and C_4 methylene groups appearing 54 p.p.b. higher at 1.245 p.p.m. The primary

group resonance at δ = 0.880 p.p.m. was similar to previous alkanes thus an alpha shift of -20.0 p.p.b. and a beta shift of -9.5 p.p.b. was again assumed in assigning the various resonances in this grouping. The mass spectral analysis of the lightly exchanged molecule examined by ^2D nmr is given in table 5.13 and the estimated rate of exchange over platinum is given in figure 5.1.

The nmr of the primary deuterium resonances was very similar to that found for n-butane exchanged over platinum, figure 5.9(c), with the first large resonance due to the grouping CH_2DCH_2- followed by minor resonances before the very large resonance caused by the CD_3CD_2- grouping in multiply-exchanged products. This reflects the deuterium distribution found by mass spectrometry. As shown in table 5.4 there were more relative amounts of exchange in the secondary than in the primary positions of n-pentane. Although the resonances for the secondary deuterium atoms in the nmr spectrum proved to be broad the disparity between the methylene groups allowed the estimated amount of exchange to be assigned further as 1.32 and 1.20 for the central and outer methylene groups respectively. Also, as the amount of d_1-product was not fully accounted for the percentage of deuterium in the CH_2DCH_2- resonance it seems that some initial alkyl reversal must occur in the methylene groups. There is some evidence from the nmr spectrum that this occurs

preferentially in the central carbon.

2,3-Dimethylbutane exchange over rhodium was examined to further investigate the tendency of this metal to promote $\alpha\gamma$- as well as $\alpha\beta$-exchange. If exchange occurred by the former process the amount of deuterium incorporated in the tertiary positions would be limited compared to the amount that may be introduced by an $\alpha\beta$-process. The mass spectral analysis shows that there was a maximum at the perdeutero-product, table 5.13, and from the relative amounts of exchange in each position, as found by the nmr analysis, table 5.4, it is clear that the tertiary position contained more deuterium than the primary position.

5.7 DISCUSSION

5.7.1 Rates

Although some kinetic data are given in figure 5.1 the quantitative information that can be derived from the results is limited, especially for palladium and iridium. Apart from propane the other three alkanes studied over the supported palladium sample appear to have a common activation energy (49±11 $kJmol^{-1}$). As will be discussed later this metal may promote exchange via formation of a π-allyl intermediate which could be facilitated by methyl group induction which is present with 2-methylpropane, n-butane and 2-methylbutane but not with propane. Over iridium all four alkanes have a similar activation energy

(38±9 $kJmol^{-1}$), this value agrees reasonably well with that found for 2,2-dimethylpropane exchange over Ir/Al_2O_3[8]. Although a similar activation energy has been reported for the same reaction over Ir/SiO_2[9] comparison of the initial product distributions over the two samples at a common temperature shows that the alumina-supported results are very much dominated by the d_1-product and subsequently the multiplicity of exchange was very much less than for the Ir/SiO_2 sample. Also, previous work investigating alkane exchange over γ-alumina[10] reported activation energies of 36, 33 and 35 $kJmol^{-1}$ for propane, 2-methylpropane and n-butane exchange respectively over similar temperature ranges. Comparison of the rates, calculated on a per gram catalyst basis, shows that the rates of exchange of propane and 2-methylpropane reported in this work were approximately an order of magnitude greater than those previously reported[10] whereas the rates of butane exchange were similar. It must therefore be concluded at this stage that the results found in the present work over the Ir/Al_2O_3 catalyst are in the main dominated by the alumina support.

The variety of alkanes exchanged over the rhodium and platinum catalysts appear to have similar activation energies of 52 and 56 $kJmol^{-1}$ respectively. With rhodium however, the results for 2-methylbutane and 2,3-dimethylbutane were not fully consistent with the other alkanes. In contrast the results for all the

alkanes exchanged over platinum lie close to a common Arrhenius line indicating that the same exchange mechanism is operative for each of the reactants over this metal. The results in figure 5.1 permit a comparison of the relative activities of the four metals for exchange of linear and branched hydrocarbons. The ratios of the activities at 333K, ignoring any differences in the degree of dispersion of the catalysts, are 291:200:27:1 for Ir:Rh:Pt:Pd. These ratios are in broad agreement with results from earlier studies[11] where a factor of 20 was found between the activity of Rh and Pt for the exchange of propene and n-butane at 311K.

5.7.2 Palladium and Platinum

From the data presented in table 5.7 the $\alpha\beta$-process adequately explains the results for the multiple-exchange of propane over palladium or platinum. It is not necessary to also invoke an $\alpha\beta\gamma$-process (π-allyl) although the possibility that it makes some contribution cannot be totally excluded. Lebrilla and Maier[12] suggested that the main mechanisms over platinum are stepwise-exchange (for primary hydrogen) and an $\alpha\beta\gamma$-process (for multiple exchange) with little role for an $\alpha\beta$-process. Their combination of mechanisms provides a possible explanation of the significant proportion of monodeuteroproducts for the reactions of hydrocarbons over platinum. It is significant however that the d_1-compound is a major

product for the exchange of ethane on platinum[13]. The production of a singly-exchanged species seems to be a general feature of platinum rather than a consequence of the relative rates of the $\alpha\beta$- and $\alpha\beta\gamma$-processes. The data of figure 5.7 suggest that an $\alpha\beta$-process can also explain the results with 2-methylpropane with the grouping of CD_3CH- in the ^2D nmr spectra being readily accounted for by isotopic dilution.

The relative amounts of exchange in the various positions of the alkanes, table 5.4, for palladium show the efficiency of this metal for promoting exchange by either an $\alpha\beta$- or an $\alpha\beta\gamma$-process. The presence of large amounts of perdeuteroproduct as shown by the mass spectrometric and ^2D nmr analyses, the case for both supported palladium samples, is compatible with such a model. Only with propane does platinum exchange the hydrogens to a similar extent. It seems that as the complexity of the alkane increases platinum tends to favour the internal hydrogens and the 2-methylbutane data show that there is relatively more exchange in the tertiary than the secondary positions. The results where monodeuteroproducts existed to the same extent in primary and secondary positions contrast with those reported by Lebrilla and Maier[12]. They claimed that the monodeuterohexane formed over platinum under the experimental conditions contained mainly primary deuterium.

5.7.3 Iridium

The Ir/Al_2O_3 catalyst exhibited a high propensity for exchange of the primary hydrogens with a very small amount of multiple-exchange for all the hydrocarbons examined. This was probably caused by exchange occurring on the alumina support as previously discussed. This would be expected to exhibit stepwise exchange[10]. The slightly larger values than unity found, were attributed to exchange occurring on the iridium although this was insufficient to significantly affect the overall distribution of products.

5.7.4 Rhodium

This metal also gave, with all the hydrocarbons studied, some monodeuteroproduct from contribution from a stepwise exchange; in all cases this was less than that found for platinum but more than for palladium. The extent of multiple-exchange was also intermediate between the values found for platinum and palladium, however with propane and 2-methylpropane the formation of multiply-exchanged products could not be explained solely by an $\alpha\beta$-process as found for these two metals. With propane it was necessary to assume contributions from an $\alpha\gamma$-process and the existence of this mechanism of multiple-exchange was confirmed with 2-methylpropane where a contribution of 19% from an $\alpha\gamma$-process was required to explain the results. However as the length of the

hydrocarbon chain increased the relative amounts of exchange in each position proved to be similar to the values found for palladium, table 5.4, thus it would seem that the ability of rhodium to promote $\alpha\gamma$-exchange with propane and 2-methylpropane becomes less as the length of the hydrocarbon chain increases.

5.7.5 Isotopic Shifts

Table 5.14 shows, in summary form, the values of the deuterium isotopic shifts which could be unambiguously assigned as observed in this and previous work[7,13]. Using these values the nmr analyses of the hydrocarbons not included in the table could also be readily interpreted. All the shifts are to low frequency, i.e. negative, and most of the alpha and beta shifts given were determined from the average of about five samples. The gamma shifts were only obtainable indirectly and for samples which contained several gamma deuterium neighbours. The probable error of the shifts is no greater than ±0.5 p.p.b. Alpha shifts for primary deuterium atoms are around -20 p.p.b. The most marked variation is the change in the alpha shift of the secondary deuterium for propane, where bond rotation is essentially free, to that for cyclopentane, where rotation is restricted. Although not included in the table but alluded to earlier is the observation that the β-shift of a secondary deuterium in n-butane is dependent on whether the interaction is with a

Table 5.14

Deuterium Isotopic Shifts Caused by Atoms Separated by two (α-shifts), three (β-shifts) or four bonds (γ-shifts)

	Deuterium Isotopic Shifts(-Δδ/p.p.b.)		
	α	β	γ
For Primary D in			
ethane[a]	19.2	8.5	-
propane	20.0	9.5	0.9
2-methylpropane	20.9	8.5	1.2
2,2-dimethylpropane[b]	20.7	-	1.5
For Secondary D in			
propane	21.2	8	-
cyclopentane[c]	17.9	7.0/8.3[d]	1.9/0.3[d]
For Tertiary D in			
2-methylpropane	-	7.6	-

a From ref. 13

b From following chapter

c From ref. 7

d Values for *cis/trans* respectively.

deuterium neighbour in the primary position or in the secondary position. It must also be noted that in general the value of the beta shift reduces as the observed deuterium nuclei change from primary to tertiary.

5.8 CONCLUSIONS

Some conclusions about the catalytic behaviour of the hydrocarbons can be summarised:

Palladium and Platinum. Both metals promote $\alpha\beta$-exchange resulting in large amounts of perdeuteroalkane; platinum also gives a significant amount of d_1-alkane from simple alkyl reversal resulting at a 'typical' U-shaped deuterium distribution.

Iridium. Results for this metal remain inconclusive for the linear and lightly branched alkanes, the high preferential primary hydrogen exchange being a consequence of the alumina support.

Rhodium. This metal promoted both $\alpha\beta$- and $\alpha\gamma$-exchange processes. The latter being especially prominent in the reactions of propane and 2-methylpropane.

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CHAPTER 6

MECHANISTIC STUDIES OF HYDROCARBON EXCHANGE REACTIONS OVER SUPPORTED METAL CATALYSTS

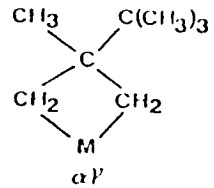
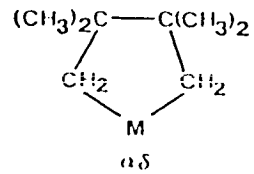
II Alkanes Containing Quaternary Carbon Atoms

6.1 INTRODUCTION

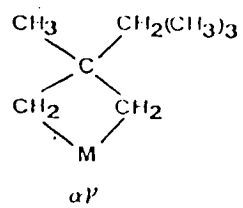
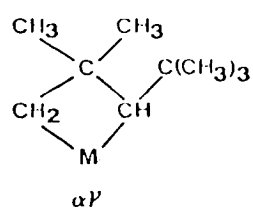
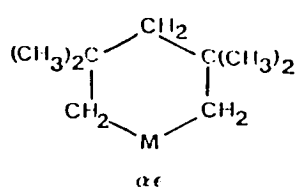
As shown in the previous chapter the use of linear or slightly branched hydrocarbons leads to extensive multiple exchange on platinum, rhodium and palladium supported catalysts. With 2,2-dimethylpropane (DMP), which contains a quaternary carbon atom, however, the number of possible intermediates is restricted and the types of multiple exchange are limited. Previous studies[1,2] with this molecule have shown that it exchanges with deuterium by one or more of three processes. The first of these, process I, involves stepwise exchange through the reversible formation of an adsorbed alkyl radical. Process II gives multiple exchange limited to a single methyl group through interconversion between adsorbed alkyl and $\alpha\alpha$-diadsorbed species. Process III, which only becomes significant at higher temperatures, leads to the formation of initial products containing deuterium atoms in two or more methyl groups, and requires interconversion of adsorbed alkyl radicals and $\alpha\gamma$-diadsorbed species. It was envisaged that the application of deuterium nmr would provide evidence in support of the three processes

described and indicate to what extent each was catalysed by the four supported metals: platinum, palladium, iridium and rhodium. As rhodium proved to be very efficient at $\alpha\gamma$-exchange, process III, more extensive studies were made with this metal to determine the influence of deuterium pressure on the individual processes.

It was also of interest to extend these studies to other quaternary carbon containing hydrocarbons. Kinetic studies, using conventional mass spectrometric techniques, were therefore carried out to compare the behaviour of DMP, 2,2,3,3-tetramethylbutane (TMB) and 2,2,4,4-tetramethylpentane (TMP) in reactions with deuterium on the four supported metal catalysts. As well as the simple exchange processes already discussed for DMP, $\alpha\gamma$-exchange with TMB would be limited to the three methyl groups attached to one of the central carbon atoms, see Scheme 6.1. If multiple exchange was to propagate beyond this $\alpha\delta$-diadsorbed intermediates, process IV, would have to be formed. With TMP extensive multiple exchange might occur through the formation of $\alpha\gamma$-adsorbed intermediates if reversible dissociation of C-H bonds, both in the methyl groups and the central methylene group, were possible, see scheme 6.2. Formation of the $\alpha\gamma$-species involving this central group would allow the exchange process to propagate over the whole molecule. Alternatively if the exchange of the methylene group was unlikely either for steric reasons or because of the intervention of

PROCESS	INTERMEDIATES	PRODUCTS
III	 $\alpha\gamma$	$(CX_3)_3CC(CH_3)_3$ -single side exchange
IV	 $\alpha\delta$	$(CX_3)_3CC(CX_3)_3$ -both sides exchange (X=H or D)

Scheme 6.1 Possible processes for exchange of 2,2,3,3-tetramethylbutane

PROCESS	INTERMEDIATES	PRODUCTS
III	 $\alpha\gamma$	$(CX_3)_3CCH_2C(CH_3)_3$ -single side exchange
III	 $\alpha\gamma$	$(CX_3)_3CCX_2C(CX_3)_3$ -exchange over whole molecule
V	 $\alpha\epsilon$	$(CX_3)_3CCH_2C(CX_3)_3$ -both sides exchange only (X=H or D)

Scheme 6.2 Possible processes for exchange of 2,2,4,4-tetramethylpentane

isomerisation reactions then the only means of extending multiple exchange beyond three methyl groups with TMP would be through $\alpha\varepsilon$-diadsorbed intermediates. A comparative study of the behaviour of DMP, TMB, and TMP in exchange reactions should therefore provide clear evidence of the relative importance of $\alpha\gamma$-, $\alpha\delta$-, and $\alpha\varepsilon$-intermediates on the four supported metal catalysts. The deuterium nmr technique was also utilised in these studies.

6.2 EXPERIMENTAL

For these studies both the static (line 1) and recirculating (line 3) vacuum systems were used. Most of the experiments with DMP and TMB were carried out on line 1. The usual reaction mixture for experiments which were not to be analysed by nmr spectroscopy was an 8:1 ratio of deuterium:hydrocarbon and a hydrocarbon pressure of 693 Pa, giving 3.5×10^{19} molecules in the reaction vessel. In experiments where examination by deuterium nmr was planned a larger charge of hydrocarbon was used, i.e. 4.3 KPa (equivalent to 2.0×10^{20} molecules) with a 5:1 ratio of deuterium:hydrocarbon. All the experiments with TMP were carried out in line 3 where a larger volume of the recirculating system was used, i.e. 1240 cm^3. This larger volume was necessary for runs with TMP as the vapour pressure was insufficient to give sufficient material in the static or normal recirculating system for

subsequent analysis by nmr spectroscopy. In the larger volume an 8:1 ratio of deuterium:hydrocarbon was used with a hydrocarbon pressure of 733 Pa giving 2.1×10^{20} molecules in the apparatus.

The catalysts used in these studies were the same as those described in section 5.2.

The course of the exchange reactions for all three hydrocarbons was followed by monitoring the amounts of pseudo-parent ions formed via loss of a methyl group from the molecules in the mass spectrometer - using 35 eV electrons to bring about ionisation. The usual corrections were made for naturally occurring isotopes and for fragmentation to other ions. A further small but important correction had to be made with TMB and TMP which was associated with the formation of parent ions. With TMB the peak at m/e 114 had to be corrected for the parent ion, $C_8H_{18}^+$, amounting to 0.28% of the pseudo-parent ion, to obtain the contribution from $C_7D_{15}^+$. The corresponding correction with TMP for the presence of $C_9H_{20}^+$ amounted to 1.25% of the pseudo-parent ion. This was subtracted from the peak at m/e = 128 to establish the contribution from $C_8H_2D_{15}^+$.

6.3 RESULTS FOR 2,2-DIMETHYLPROPANE EXCHANGE AND INTERPRETATION OF ^2D NMR SPECTRA

The mass spectrometric analyses of the various samples subsequently examined by nmr spectroscopy are given in table 6.1. In the majority of experiments the reaction was stopped after approximately 15% of the light ion, $C_4H_9^+$, had been exchanged in order to obtain products where most of the molecules had only reacted once. In one experiment, PTDMP2E, an equilibrated mixture of a high deuterium content was obtained by reacting the alkane and deuterium for some hours over the platinum catalyst, condensing the hydrocarbon, replacing the hydrogen/deuterium mixture with fresh deuterium and continuing the reaction. The agreement between the mass spectrometric analysis for this experiment and the corresponding calculated distributions for a random distribution of hydrogen and deuterium atoms in the ions, shown in the last column of table 6.1, confirmed the validity of the mass spectrometric analyses.

Most of the nmr spectra for DMP were comparatively simple and gave well separated resonances for $-CH_2D$, $-CHD_2$ and $-CD_3$ as shown by the results for the experiment IRDMP2, figure 6.1. The resonance of highest frequency corresponding to the $-CH_2D$ grouping occurred at δ = 0.918±0.005 p.p.m. with the shift in resonance for an additional deuterium atom in the same methyl group having a value of α = -20.7±0.003 p.p.b. and the corresponding

Table 6.1

Mass Spectrometric Analyses of 2,2-Dimethylpropane Subsequently Examined by ^2D nmr

Expt.	PDDMP2	Calc.[a]	IRDMP2	RHDMP2	PTDMP1	PTDMP2E	Calc.[b]
Catalyst	Pd(B)		Ir	Rh	Pt	Pt	
T/K	460		450	450	431	450	
Deuterium Content							
D_0	79.71	79.18	83.27	85.87	85.56	-	
D_1	17.72	18.72	13.32	5.30	8.06	-	
D_2	2.35	1.97	2.43	2.09	3.20	-	
D_3	0.22	0.12	0.63	1.71	1.66	-	0.03
D_4	-	0.05	0.15	1.10	0.80	0.64	0.30
D_5	-	-	0.06	0.88	0.37	2.45	1.95
D_6	-	-	0.02	0.87	0.18	8.48	8.43
D_7	-	-	0.02	0.88	0.09	22.30	23.50
D_8	-	-	0.02	0.80	0.05	36.70	38.20
D_9	-	-	0.08	0.50	0.03	29.41	27.60
M_d^c	0.231	0.231	0.221	0.457	0.269	7.80	7.80
M_X^d	1.14	-	1.32	3.23	1.86	7.80	-

a Calculated distribution with 0.23 D atoms per ion for comparison with PDDMP2.

b Calculated distribution with 7.80 D atoms per ion for comparison with PTDMP2E.

c M_d is the mean deuterium content of the $C_4X_9^+$ ions.

d M_X is the mean number of deuterium atoms int he $C_4X_9^+$ ions from exchanged molecules.

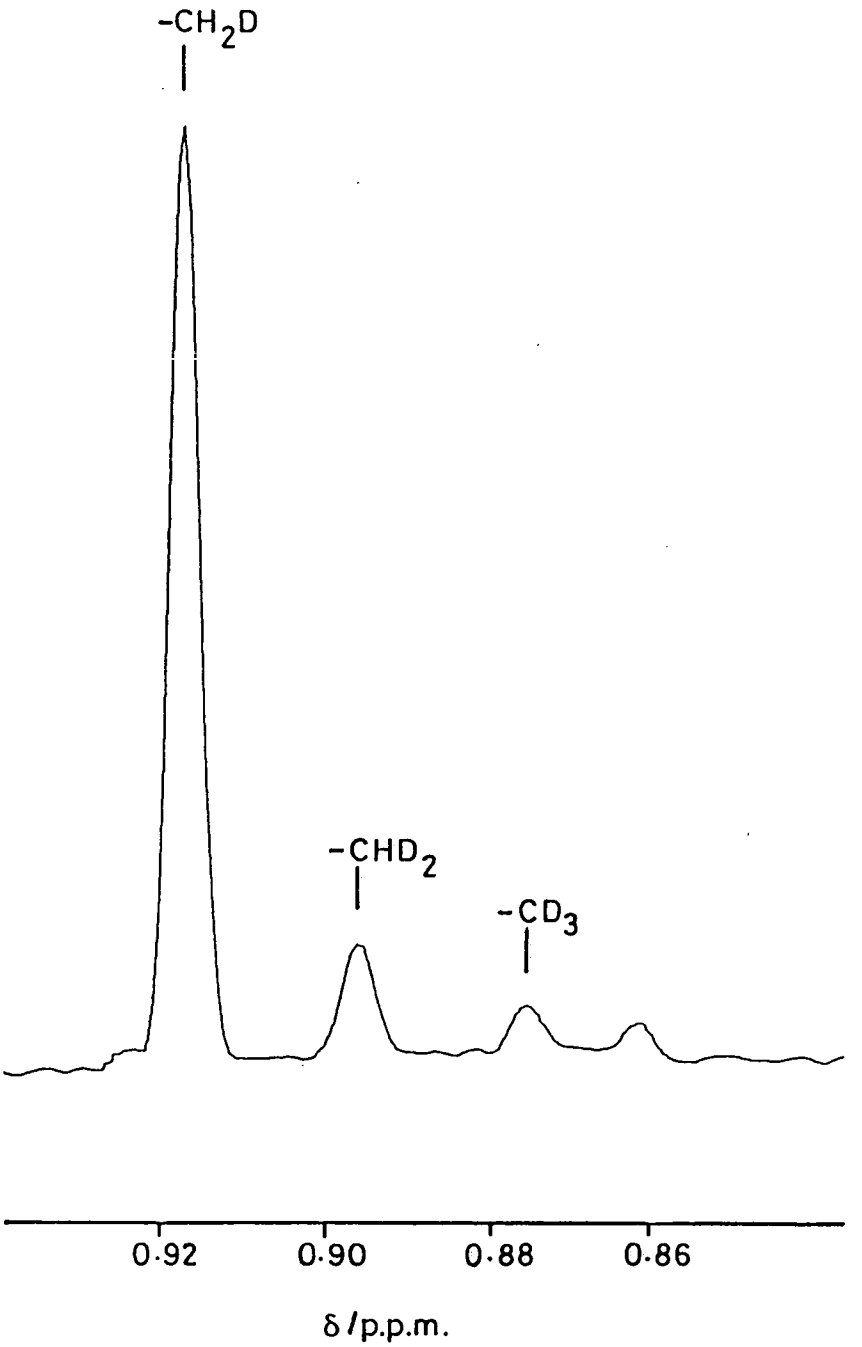


Figure 6.1 ^{2}D nmr spectra of exchanged 2,2-dimethylpropane over Ir/Al_2O_3 at 450K.

shift for two such deuterium atom neighbours being 2α = -41.4±0.006 p.p.b. The spectrum of the equilibrated sample from experiment PTDMP2E also showed resonances due to methyl groups with one, two, or three deuterium atoms as indicated in figure 6.2 (a) with the major peak corresponding to $-CD_3$ because of the high degree of exchange. An estimate of the gamma shifts caused by deuterium atoms in other methyl groups was obtained by running a spectrum of a mixture of a small fraction of the enriched sample from experiment PTDMP2E with a large fraction of a lightly exchanged sample obtained from an experiment using γ-Al_2O_3 as the catalyst, which had previously been shown to exchange DMP in a stepwise manner. The nmr spectrum of the mixture is given in figure 6.2 (b) and four clear peaks were identified, table 6.2.

Inspection of the results in this table indicates values for the xγ-shifts of -11.3 p.p.b. and -11.4 p.p.b. The ions formed from the equilibrated sample contained on average 7.80 atoms in the three methyl groups and it is therefore probable that each deuterium atom in the parent molecule had the same average number of deuterium neighbours in the γ-position, i.e. the average of x = 7.8. Hence the γ-shift per deuterium atom = -1.5 p.p.b. The main reasons why the nmr spectra for DMP proved to be comparatively simple was (i) the absence of any β-deuterium nuclei because each methyl group is bonded

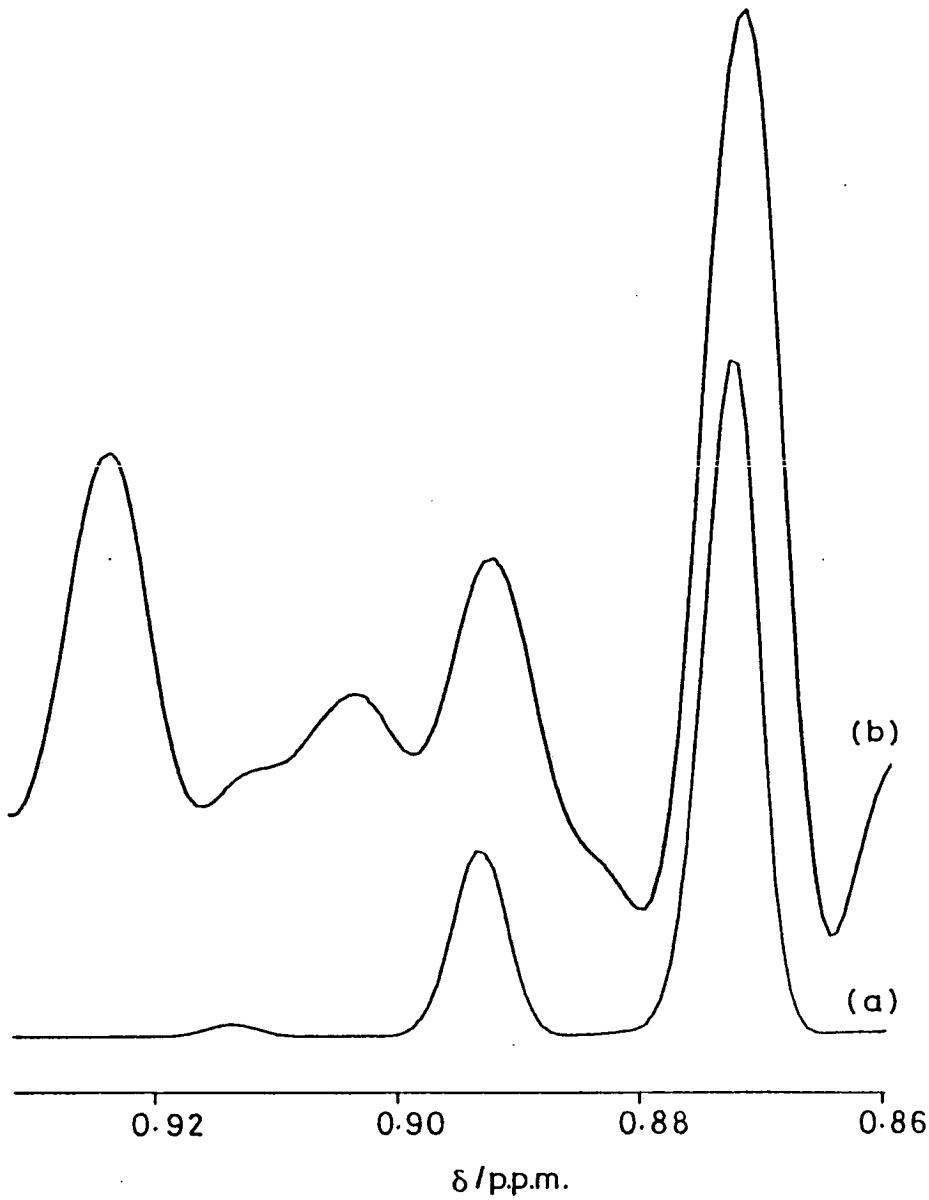


Figure 6.2 ^{2}D nmr spectra of exchanged 2,2-dimethylpropane

(a) heavily exchanged sample (PTDMP2E)

(b) mixture of heavily and lightly exchanged samples.

Table 6.2

Resonances in the ^2D nmr Spectrum of the Mixture of Lightly Exchanged and Heavily Exchanged 2,2-Dimethylpropane

Methyl Group	δ/p.p.m.	$-\Delta$/p.p.b.	Isotopic Shifts for $\Delta\delta$
$-CH_2D$[a]	0.90279	-	
$-CHD_2$[a]	0.9075	20.4	α
$-CHD_2$[b]	0.8962	31.7	$\alpha + \chi\gamma$
$-CD_3$[b]	0.8757	52.2	$2\alpha + \chi\gamma$

a from lightly exchanged 2,2-dimethylpropane over γ-Al_2O_3.

b from heavily exchanged 2,2-dimethylpropane over Pt(PTDMP2E).

Table 6.3

Relative Amounts of $-CH_2D$, $-CHD_2$ and $-CD_3$ in Equilibrated Molecules

	$-CH_3$	$-CH_2D$	$-CHD_2$	$-CD_3$
Relative amount of the groups	h^3	$3h^2d$	$3hd^2$	d^3
Relative amount of deuterium atoms	0	$3h^2d$	$6hd^2$	$3d^3$

only to the quaternary carbon atom in the molecule and (ii) the large value of the α-shift in comparison with the γ-shift.

As well as the normal resonances for $-CH_2D$, $-CHD_2$ and $-CD_3$, A, B, and D respectively in figure 6.3 (b), the spectrum from DMP exchange over rhodium at 450K showed two additional resonances, peaks C and E. These were assigned to $-CHD_2$ and $-CD_3$ groups in molecules substantially exchanged in the other three methyl groups resulting in a detectable separate resonance through the combined influence of several γ-shifts.

As table 6.1 shows the agreement between the experimental distribution for palladium and that predicted assuming a stepwise reaction is reasonably close. Further confirmation for a stepwise mechanism over this metal was obtained by correlating the results from the nmr spectrum with the measured amounts from mass spectrometry. In stepwise exchange the deuterium in the hydrocarbon would be randomly distributed. The chance of finding a deuterium atom in any position will be $d = M_d/9$ and the corresponding chance of having a hydrogen atom (h) will be 1-d. The expected relative amounts of the methyl groups and of the deuterium atoms in these groups are set out in table 6.3 and as the results in table 6.4 demonstrate reasonable agreement was obtained.

Although the other metals exhibited multiple exchange, as indicated by the mass spectrometric analyses in table

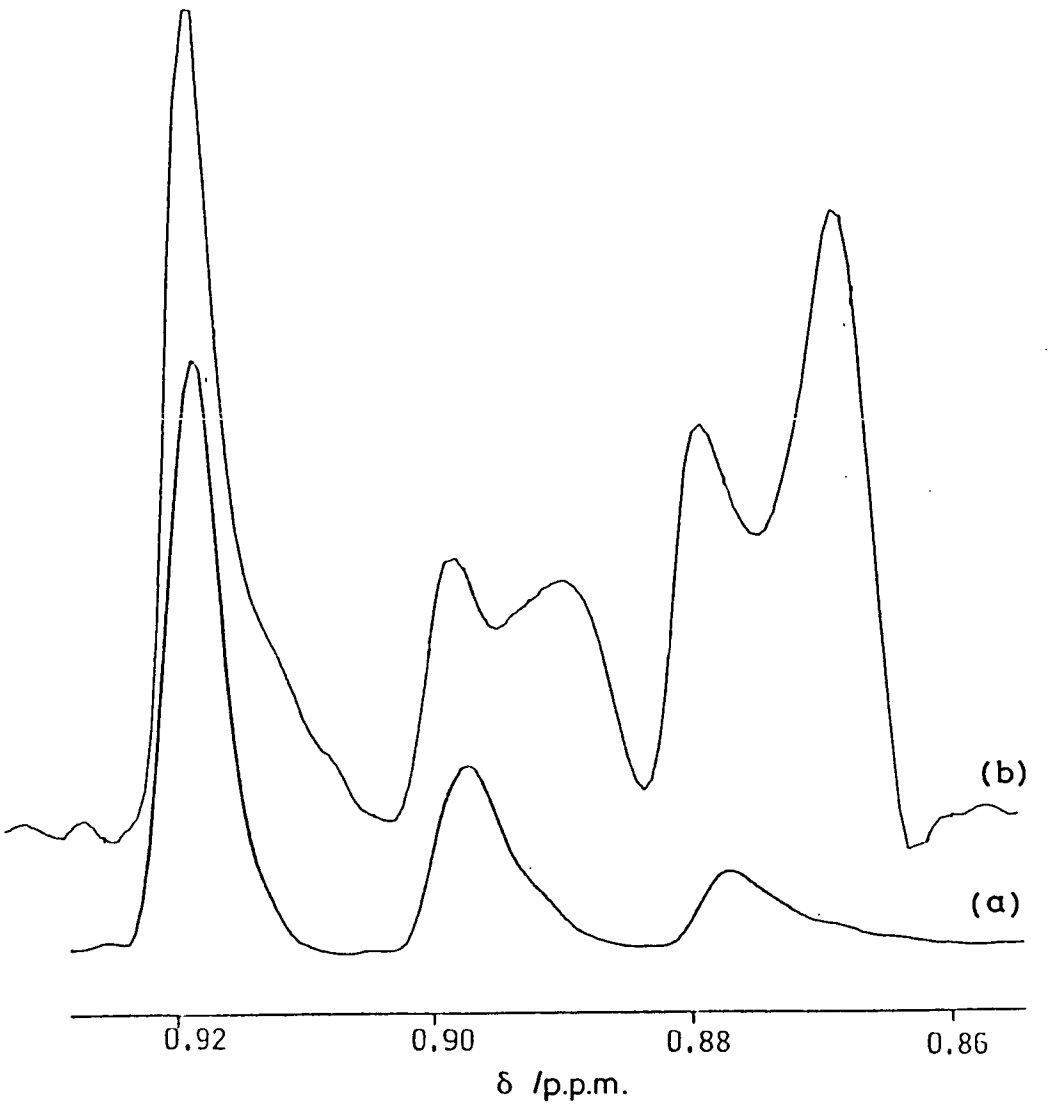


Figure 6.3 ^{2}D nmr spectra of exchanged 2,2-dimethylpropane

(a) DMP exchange (14.4%) over Pt/SiO_2 at 450K (PTDMP1)

(b) DMP exchange (11.4%) over Rh/SiO_2 at 450K (RHDMP3).

Table 6.4

Distributions of Deuterium in Exchanged 2,2-Dimethylpropane

Experiment	PDDMP2	PTDMP1	IRDMP2	RHDMP2
Catalyst	Pd(B)	Pt	Ir	Rh
T/K	460	431	450	450
Grouping	Percentage of total Deuterium			
A $-CH_2D$	93 (95)[a]	63	73	28
B $-CHD_2$ without γ shifts	7 (5)[a]	25	13	7
C $-CHD_2$ with γ shifts	0			22
D $-CD_3$ without γ shift	0	12	8	9
E $-CD_3$ with γ shifts	0		6	34

a Calculated using table 6.3 with d = 0.026

6.1 with products containing up to 9 deuterium atoms, in all cases the D_1 product was present in substantial amounts. Thus stepwise exchange, process I, is a very important component of the exchange mechanism. The presence of $-CHD_2$ and $-CD_3$ peaks in the nmr spectra shows that process II, multiple exchange in one methyl group, is also an important process. This is particularly the case with platinum and although process III, $\alpha\gamma$-exchange, must also occur over this metal to give the highly deuterated products this process is not as pronounced as over both iridium and rhodium. The broadening of the methyl resonances in the ^2D nmr spectra of DMP exchange over platinum, figure 6.3(a), is believed to be caused by small amounts of γ-interactions.

In contrast, over iridium and rhodium there were substantial γ-interactions to give additional resonances, as shown in figures 6.1 and 6.3(b), with quantitative results being given in table 6.4.

6.4 COMPARATIVE STUDIES OF EXCHANGE REACTIONS INVOLVING HYDROCARBONS CONTAINING QUATERNARY CARBON ATOMS

6.4.1 Kinetic Behaviour

Experiments with the iridium, platinum or rhodium catalysts were carried out at about 393K and 423K but temperatures up to 460K were needed to obtain adequate rates with the palladium catalyst.

Data from experiments with iridium, palladium or platinum conformed to the first order reversible rate equation (equ. 3.3) as indicated by the representative plots in figure 6.4; a slight decrease in rate was apparent for the experiment with TMP on palladium at 456K but only after 250 min. However, the rates of exchange reactions using rhodium decreased with time as shown in figure 6.5, with the effect most pronounced with DMP and least noticeable with TMP.

Initial rates for all the exchange reactions are given in the Arrhenius diagram for each metal in figure 6.6. Similar rates of reaction were found for the three hydrocarbons studied, particularly over palladium which gave results with a common activation energy of 91±4 $kJmol^{-1}$. The rhodium results are based on preliminary work with TMB where the exchange reaction was studied at 344K and 363K as well as at 394K and an activation energy of 54 $kJmol^{-1}$ was calculated[3]. Likewise for iridium the results give a straight line plot with a similar shape to that found[4] for exchange of DMP over the temperature range from 301 to 452K with E = 38 $kJmol^{-1}$. With platinum, the data give an activation energy of 103±13 $kJmol^{-1}$; this value is significantly higher than the activation energy of 56 $kJmol^{-1}$ reported for an alumina-supported platinum catalyst[4].

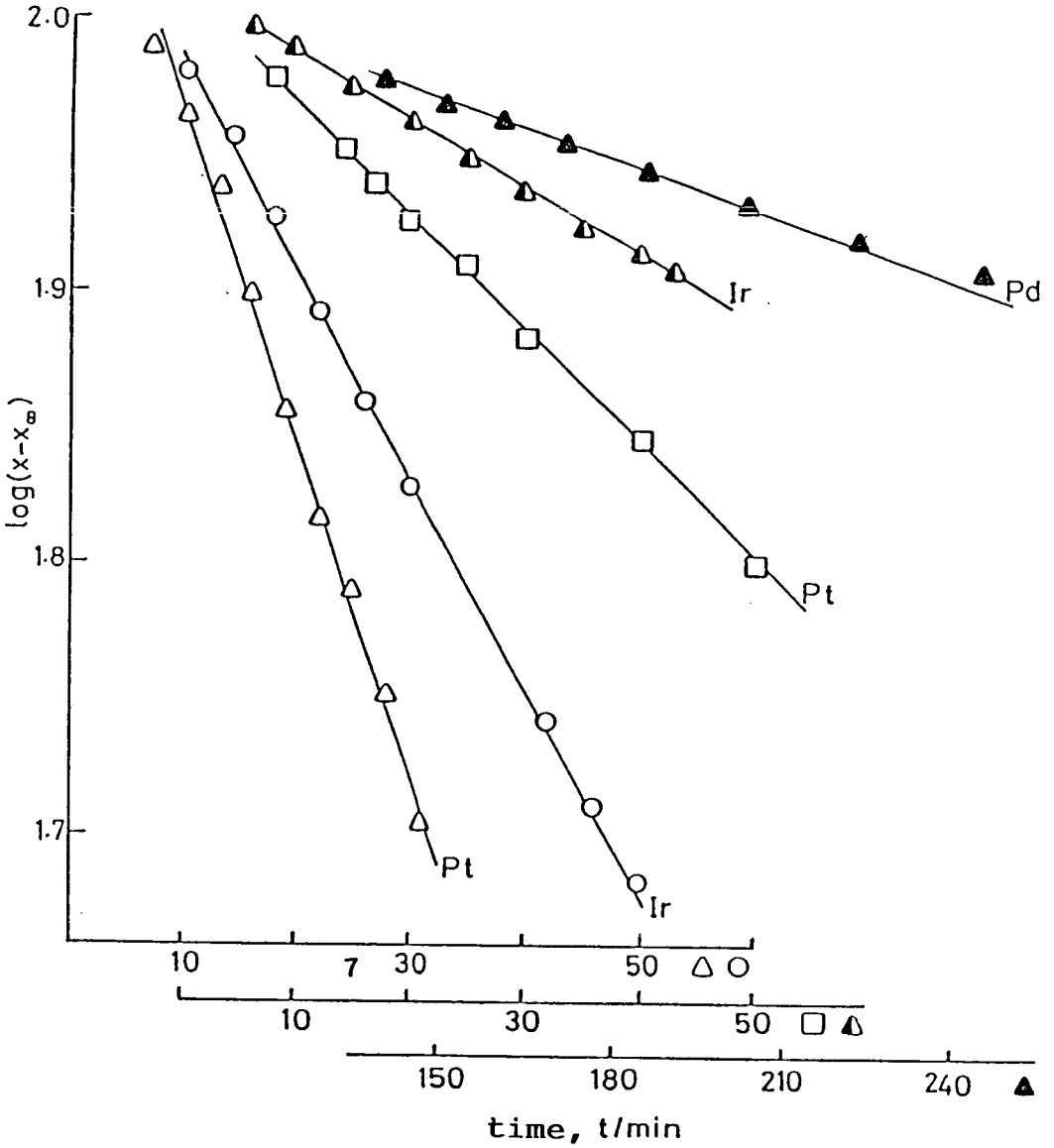


Figure 6.4 Rate plots according to equ. (3.3) for reactions over iridium, palladium and platinum : squares, DMP; circles, TMB; triangles, TMP.

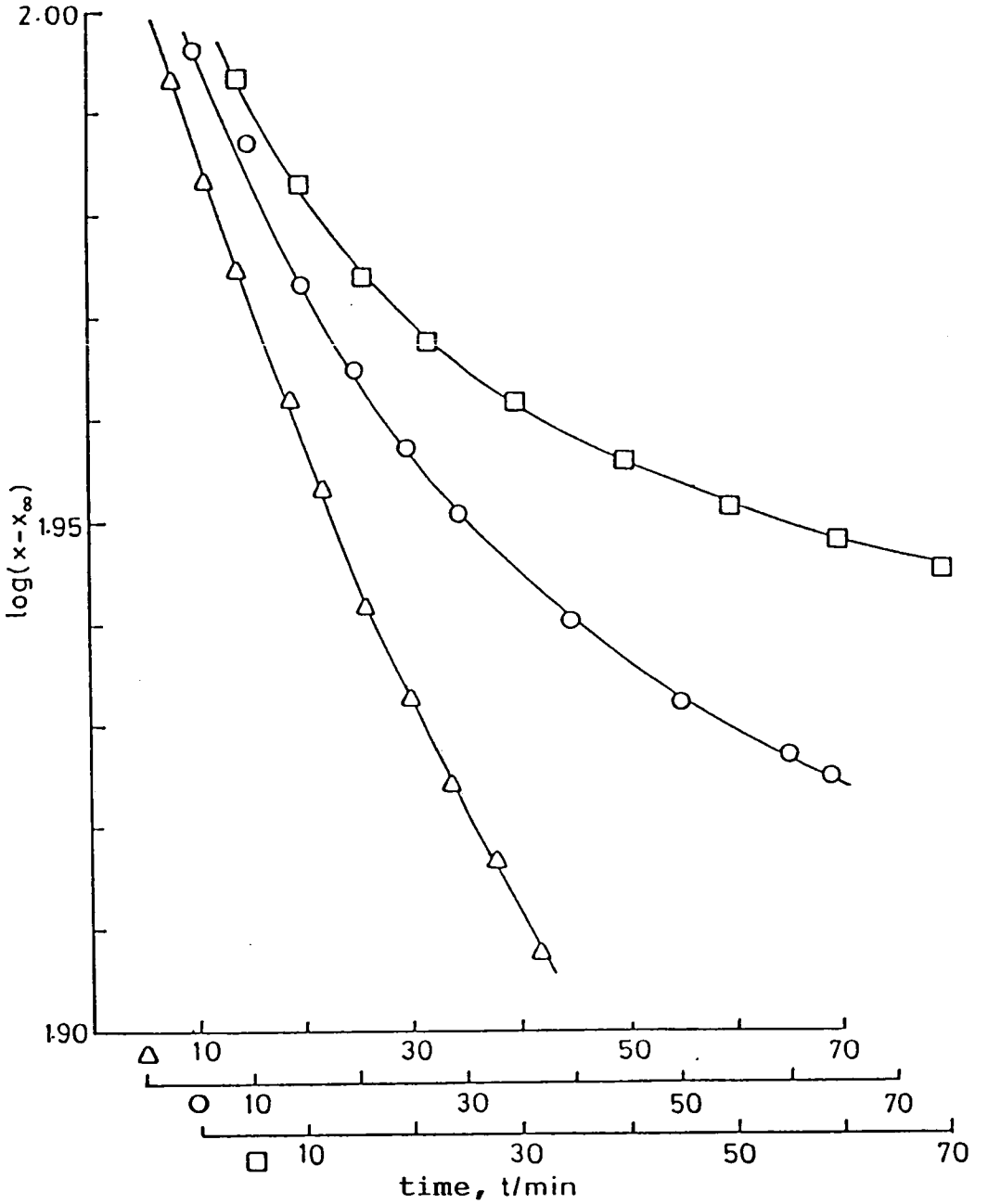


Figure 6.5 Rate plots according to equ. (3.3) for reaction over rhodium at 423K:
□ , DMP; O, TMB; Δ , TMP.

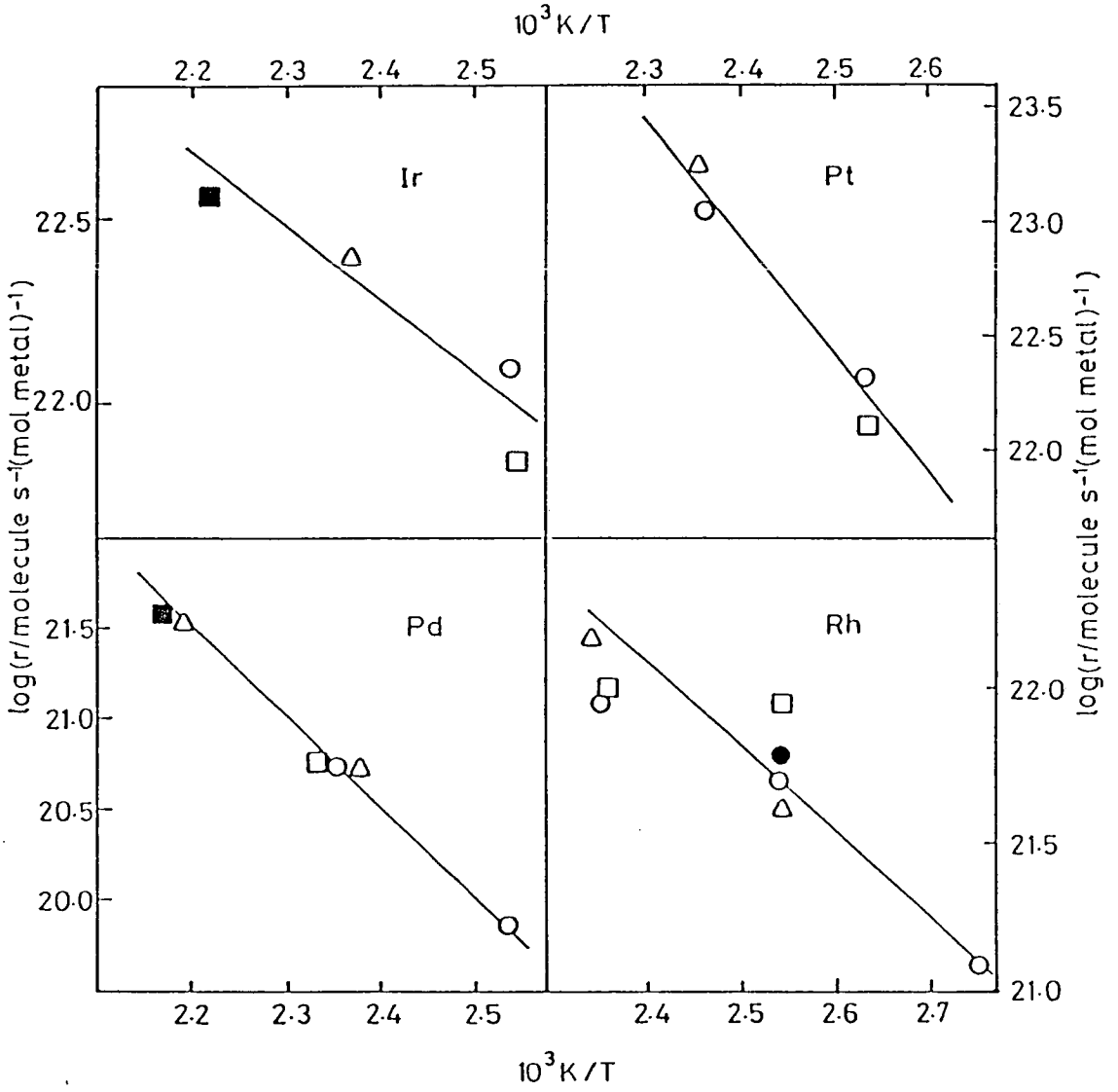


Figure 6.6 Rates of exchange plotted on Arrhenius diagrams for each of the metals : squares, DMP; circles, TMB; triangles, TMP. Filled symbols were rates from experiments on the static line (line 1) planned for nmr with the higher pressure of hydrocarbon and a 5:1 ratio of D_2:hydrocarbon.

6.4.2 Product Distributions

The product distributions for each exchange experiment, in terms of the pseudo-parent ions, were obtained from the mass spectrometric analyses at low conversions. The kinetic data were used to calculate M, the mean number of D atoms in the ions, from the initial products as described in 3.4.2. Results for palladium are given in the upper part of table 6.5. The values of M at both temperatures for DMP and 424K for TMB showed that stepwise exchange was the dominant process with these systems. This conclusion was confirmed by the agreement between the observed product distributions at 10% conversion and the calculated random distributions. With TMP at 456K, stepwise exchange was again the dominant reaction although there was a contribution from another process as well.

Results for platinum and iridium are given in table 6.6 at a conversion of 15%. This value was chosen in order to show the small amounts of the more highly exchanged products. At 15% conversion there is a significant contribution from molecules that have made two effective visits to the catalyst surface - about 14% of the molecules shall have exchanged once and 1% will have reacted twice. With iridium, some multiple exchange limited to methyl groups, i.e. process II, occurs with all three reactants but further multiple exchange contributes only to a very small extent. General multiple exchange

Table 6.5

Product Distributions for Exchange on Palladium(B)

Experiment	PDDMP1		PDDMP2	PDTMB1		PDTMP1
Reactant		DMP		TMB		TMP
T/K	429		460	424	456	
MS distribution of ions at 10% conversion		Calc. A			Calc. B	
D_1	9.54	(9.51)	9.33	9.46	(9.52)	9.05
D_2	0.43	(0.45)	0.64	0.52	(0.47)	0.62
D_3	0.03	(0.01)	0.03	0.02	(0.01)	0.11
D_4	-		-	-		0.03
M	1.00		1.03	1.03		1.16
conversion for nmr analyses			20.3			19.8
%D in groupings		Calc. C			Calc. D	
$-CH_2D$	(95)		93	(97)	88	
$-CH_2$	(5)		7	(3)	6	
$-CD_3$			-		3	
$-CD_3$ + γ shifts			-		3	

The calculated distributions A and B, for the pseudoparent ions are those expected for stepwise exchange at 10% conversion for 9 and 15 exchangeable H atoms, respectively.

Distribution C corresponds to a random distribution with a chance d=0.0256 of a D atom in each position based on the mass-spectrometrically determined average D-content of the $C_4X_9^+$ ions of 0.231.

Distribution D corresponds to a random distribution with a chance d=0.165 of a D in 15 positions based on the mass spectrometrically determined average D-content of the $C_nH_2X_{15}^+$ ions of 0.248.

Table 6.6

Product Distributions for Exchange on Platinum and Iridium at 15% Conversion

Experiment	PTDMP2	PTTMB2	PTTMB3	PTTMP3	IRDMP3	IRTMB2	IRTMP1
Catalyst		Platinum				Iridium	
Reactant	DMP	TMB		TMP	DMP	TMB	TMP
T/K	394	395	423	424	392	394	422
Composition of ions							
D_1	10.30	8.69	6.12	4.99	12.78	11.22	12.01
D_2	2.66	3.25	3.03	2.91	1.86	2.74	2.03
D_3	1.30	1.45	1.52	1.79	0.32	0.67	0.42
D_4	0.44	0.73	1.08	1.28	0.04	0.12	0.16
D_5	0.18	0.32	0.78	0.98	-	0.03	0.09
D_6	0.08	0.19	0.60	0.74	-	0.02	0.06
D_7	0.04	0.11	0.43	0.59	-	0.01	0.06
D_8	0.03	0.08	0.35	0.49	-	0.01	0.06
D_9	0.02	0.07	0.30	0.41	-	0.05	0.06
D_{10}		0.04	0.26	0.32		0.02	0.06
D_{11}		0.03	0.19	0.19		0.02	-
D_{12}		0.03	0.15	0.16		0.04	-
D_{13}		0.01	0.11	0.11		0.02	-
D_{14}		0.00	0.07	0.04		0.01	-
D_{15}		0.00	0.00	-		0.02	-
M	1.45	1.75	2.24	2.64	1.11	1.35	1.27

plays a greater part in the reactions over platinum and increases with temperature as shown by the two sets of results with TMB. Results for reactions over rhodium at 10% conversion are given in table 6.7 and show significant contributions from multiple exchange processes. The influence of temperature on the values of M for exchange over iridium, platinum and rhodium catalysts is shown in figure 6.7.

6.4.3 ^{2}D nmr Analyses of TMB and TMP

The main features associated with the deuterium nmr spectra of exchanged DMP have already been described in section 6.3

TMB. The chemical shift for the $-CH_2D$ group was $\delta = 0.865 \pm 0.007$ p.p.m., and spectra of the products from three reactions are shown in figures 6.8, 6.9 and 6.10. Small peaks from the spectra from the rhodium experiments indicated that the α-shift was about -20 p.p.b. and the total shifts for the highly exchanged molecules were -53.4 p.p.b. and -55.1 p.p.b. If the two alpha shifts account for -40 p.p.b. of these displacements the remaining -14 p.p.b. represented the combined effect of up to six gamma and nine delta shifts.

The spectrum of the relatively highly exchanged sample from the reaction over platinum at 423K, figure 6.9, shows just three slightly broadened resonances corresponding to $-CH_2D$, $-CHD_2$ and $-CD_3$ groups. The isotopic shifts

Table 6.7

Product Distributions for Exchange on Rhodium at 10% Conversion

Experiment	RHDMP5	RHDMP6	RHTMB2	RHTMB5	RHTMP1	RHTMP2
Reactant	DMP		TMB		TMP	
T/K	393	423	394	424	393[a]	426
Composition of ions						
D_1	6.80	4.18	6.47	4.82	6.24	4.32
D_2	1.30	1.35	1.22	1.13	1.17	1.13
D_3	0.95	1.29	0.42	0.51	0.49	0.62
D_4	0.36	0.72	0.14	0.17	0.25	0.39
D_5	0.18	0.51	0.05	0.15	0.25	0.43
D_6	0.12	0.44	0.03	0.14	0.21	0.36
D_7	0.10	0.44	0.04	0.18	0.21	0.43
D_8	0.10	0.52	0.09	0.29	0.33	0.61
D_9	0.10	0.55	0.22	0.31	0.25	0.51
D_{10}			0.12	0.38	0.18	0.45
D_{11}			0.13	0.40	0.21	0.42
D_{12}			0.28	0.50	0.13	0.20
D_{13}			0.16	0.41	0.05	0.10
D_{14}			0.25	0.42	-	-
D_{15}			0.35	(0.18)[b]	-	-
M	1.51	(3.2)[b]	3.79	(4.6)[b]	2.50	3.54

a The ratio of D_2:hydrocarbon in this experiment was 5:1 compared with 8:1 in the others.

b Values which were subject to greater error.

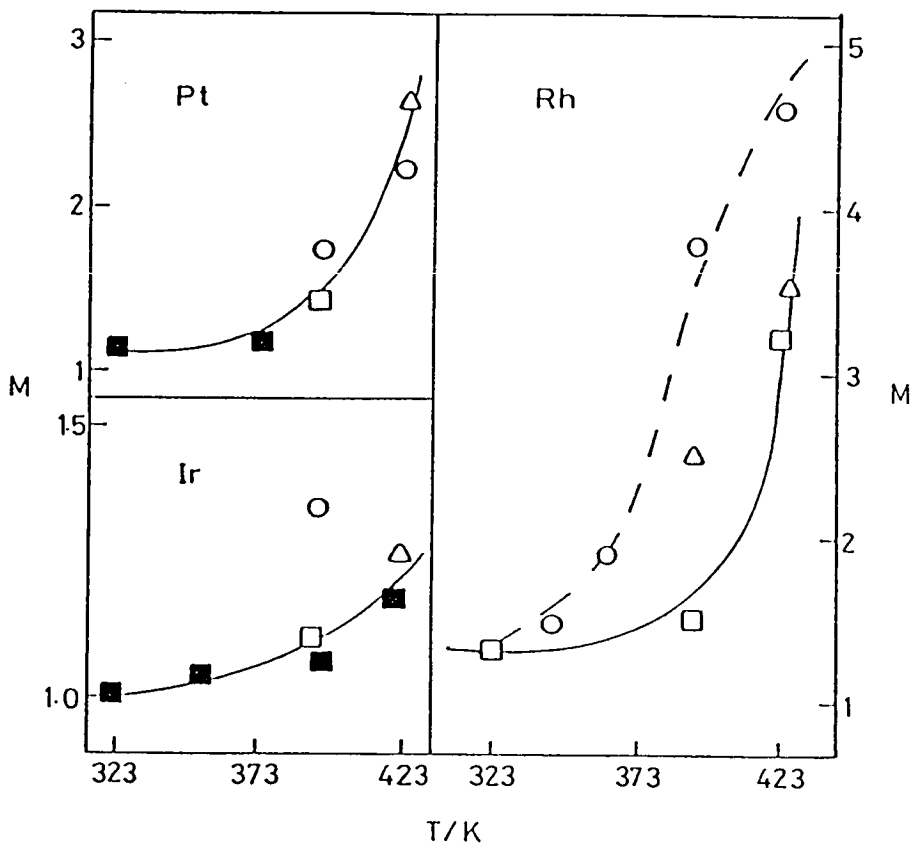


Figure 6.7 Influence of temperature on the values of M, measuring the multiplicity of exchange, for reactions on iridium, platinum and rhodium catalysts: squares, DMP; circles, TMB; triangles, TMP. Filled symbols are results obtained previously for DMP on platinum[5] or iridium[6].

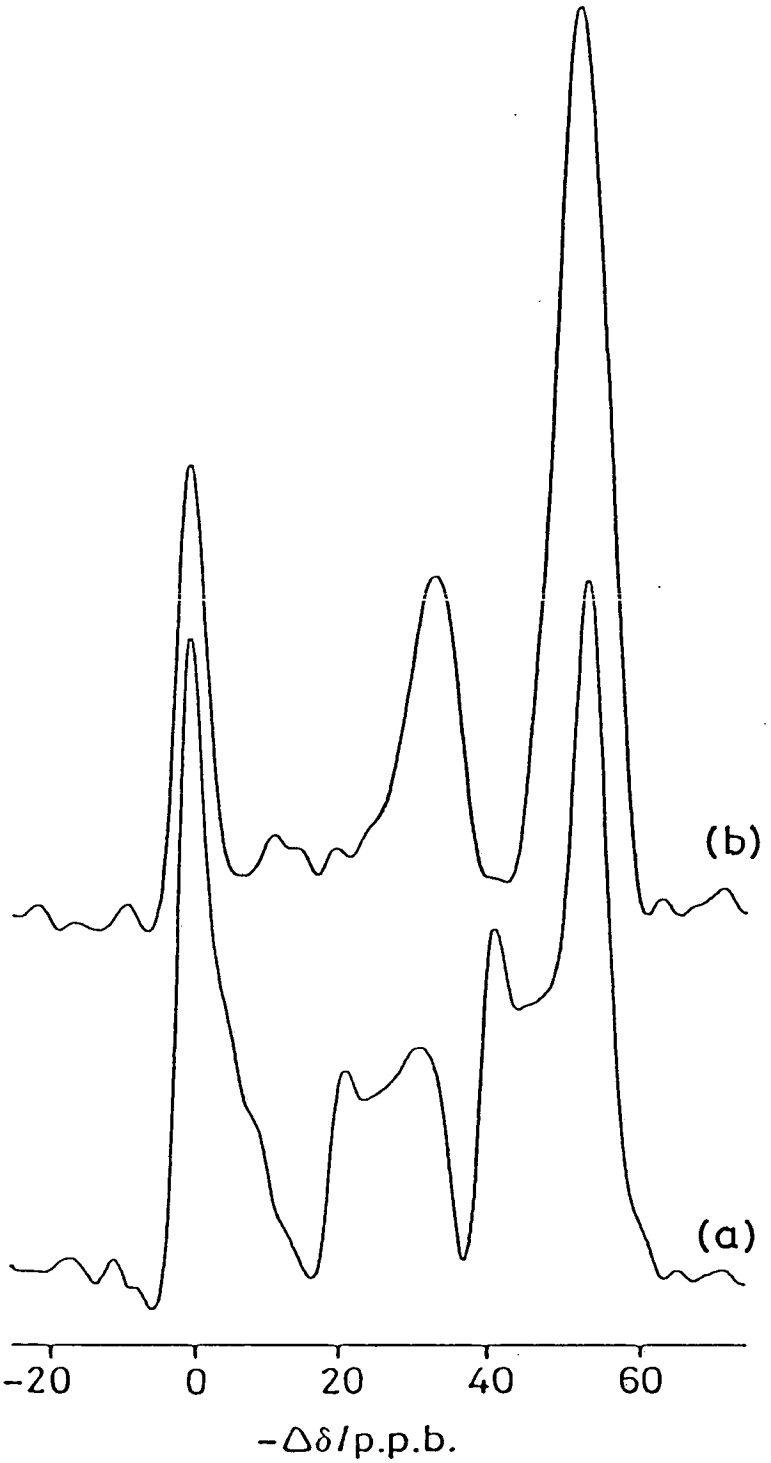


Figure 6.8 ^{2}D nmr spectra for DMP and TMNB exchanged over rhodium

(a) DMP, 12% reacted at 423K using 8:1 ratio of D_2:hydrocarbon with highest frequency at δ=0.924 p.p.m. w.r.t. TMS

(b) TMB, 15.9% reacted at 424K using 5:1 ratio of D_2:hydrocarbon and highest frequency at δ=0.869 p.p.m.

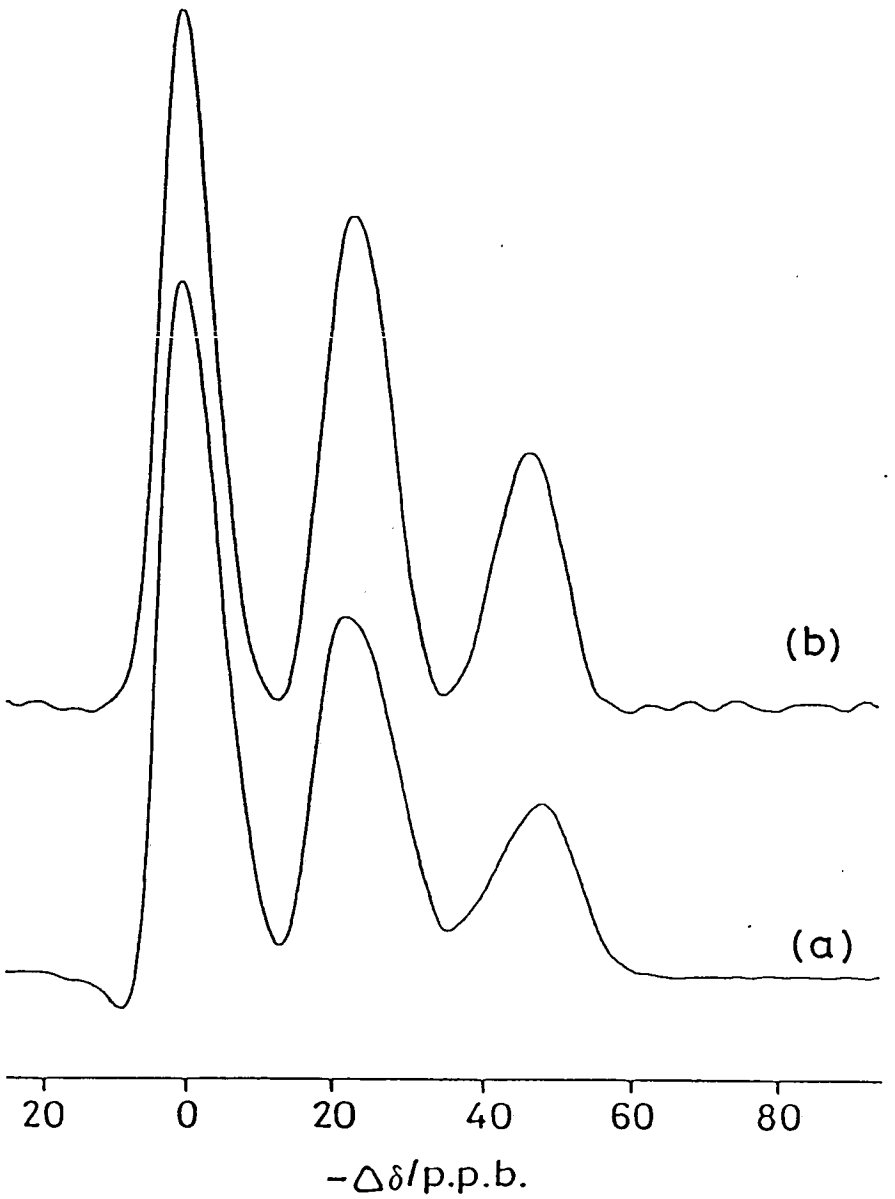


Figure 6.9 ^{2}D nmr spectra for TMB and TMP substantially exchanged over platinum.

(a) TMB, 70.3% reacted at 423K with highest frequency at δ=0.868 p.p.m. w.r.t. TMS.

(b) TMP, 49.3% reacted at 424K and highest frequency at δ=0.983 p.p.m.

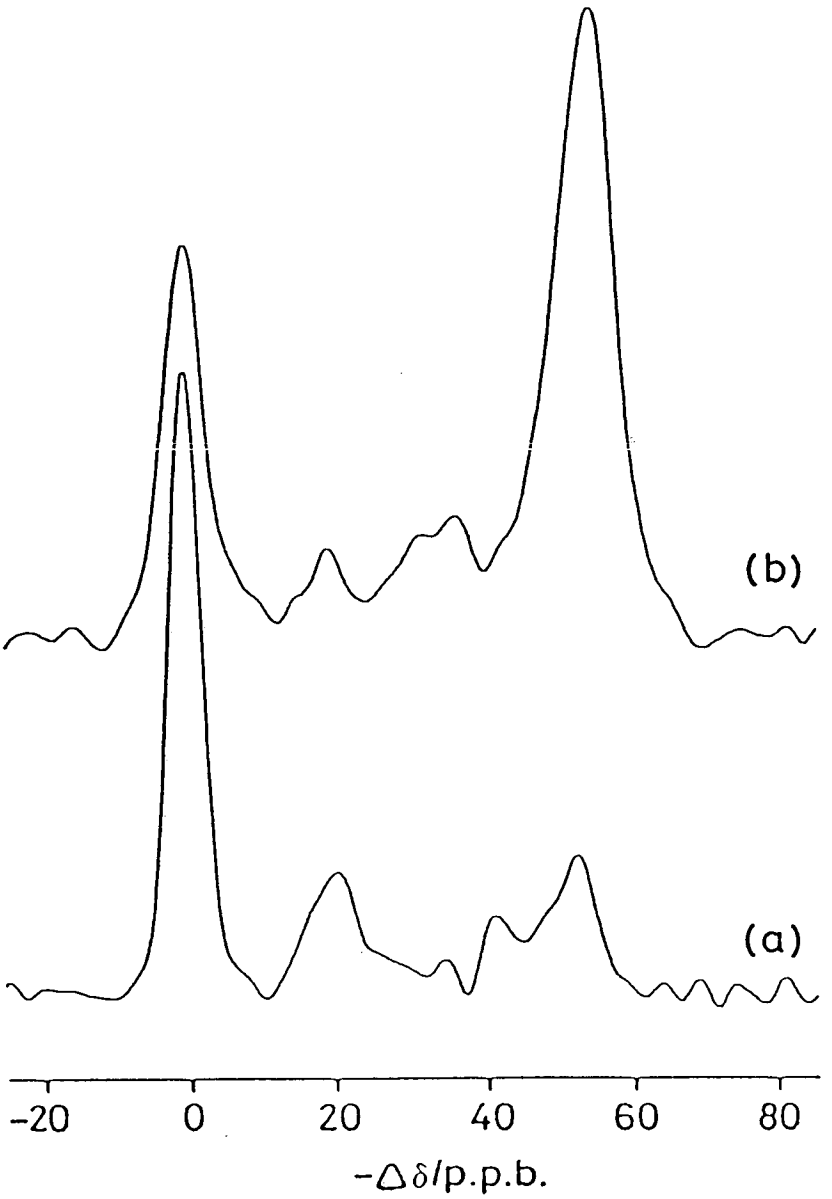


Figure 6.10 ^{2}D nmr spectra for TMB and TMP exchanged over rhodium.

(a) TMP, 15.9% reacted at 394K using a 5:1 ratio of D_2:hydrocarbon with the highest frequency peak at δ=0.979 p.p.m. w.r.t. TMS.

(b) TMB, 13.7% reacted at 394K using a 4:1 ratio of D_2:hydrocarbon and highest frequency at δ=0.858 p.p.m.

associated with the latter peaks were -22.4 p.p.b. and -48.5 p.p.b. and so they correspond to the usual alpha shifts together with small contributions from the minor gamma and delta shifts.

TMP. The chemical shift for primary deuterium in TMP was 0.979±0.007 p.p.m. A spectrum using the naturally occurring deuterium in the molecules showed that the chemical shift for deuterium in the methylene group was 1.24 p.p.m. but no exchange was detected in this position in any of the reactions. Spectra of products from exchange over palladium and iridium showed that the α-shift for the grouping $-CHD_2$ was -20.7 p.p.b., a value identical to that found for DMP. A spectrum for substantially exchanged TMP over platinum is shown in figure 6.9 and gave the usual resonances for $-CH_2D$, $-CHD_2$ and $-CD_3$ with some contributions from minor isotopic shifts as the displacements were -23.2 p.p.b. and -46.7 p.p.b.

Part of the spectrum for TMP reacted over rhodium is shown in figure 6.10; two small peaks containing 7% of the total deuterium observed by nmr were present with chemical shifts of 1.445 p.p.m. and 1.484 p.p.m. In a second experiment using rhodium, 6% of the deuterium was associated with a small peak at 1.438 p.p.m. These results show unequivocally that exchange over rhodium was accompanied by other reactions, such as isomerisation, with the peaks in the region of δ = 1.45 p.p.m.

representing secondary (or tertiary) deuterium atoms in the products. Since isomerised products would be likely to contain primary deuterium atoms they probably contributed to some of the small peaks in the spectrum, shown in figure 6.10, which was therefore not attributable solely to primary deuterium in exchanged TMP.

6.4.4 Distribution of Primary Deuterium Atoms in Products

The results for the distributions of the deuterium atoms in the different groupings for products from reaction over palladium are given in the lower part of table 6.5. The corresponding results for the same reactions over platinum and iridium are shown in table 6.8 and the more detailed analyses made for rhodium are presented in table 6.9.

6.5 DISCUSSION

6.5.1 Palladium

From the results in tables 6.1 and 6.6 for DMP it is clear that the most important reaction was stepwise exchange with good agreement between the mass spectrometric distribution of deutero-ions and the calculated random values at 429K and 460K. The calculated amount of deuterium in the $-CHD_2$ grouping of the nmr is also in good agreement with that found experimentally, table 6.6. Stepwise exchange is also important with TMB

Table 6.8

Distributions of Deuterium Atoms in the Methyl Groups in the Products from Reactions over Platinum and Iridium

Experiment	PTDMP1[a]	PTTMB3	PTTMP1	IRTMP1
Catalyst		Platinum		Iridium
Reaction	DMP	TMB	TMP	TMP
T/K	431	423	424	422
% conversion	14.4	70.3	49.3	19.0
M_X[b]	1.86	3.24	3.43	1.58
Grouping	Percentage of Total Deuterium			
$-CH_2D$	63	50	44	91
$-CHD_2$	25	34	37	9
$-CD_3$	12	16	19	0

b M_X is the mean number of deuterium atoms in the pseudo-parent ions from exchanged molecules.

a Experiment PTDMP1 used previously in Table 6.4.

Table 6.9

Distributions of Deuterium Atoms in the Methyl Groups in the Products from Reactions over Rhodium

Experiment	RHOMP6	RHTMB1	RHTMB5	RHTMP1
Reactant	DMP	TMB		TMP
T/K	423	394[a]	423	394
% conversion	12.0	13.7	15.9	15.9
M_x[b]	3.18	2.98	4.63	2.61
Grouping	Percentage of Total Deuterium			
$-CH_2D$	22.6	25.8	16.4	53.5
$-CHD_2$ + minor shifts	7.2	1.3	4.6	-
$-CHD_2$	8.6	3.6	2.0	16.5
$-CHD_2$ + minor shifts	12.8	4.5	23.0	1.4[c]
$-CD_3$	13.3	6.6	0.0	5.8
$-CD_3$ + minor shifts	35.5	58.2	54.0	15.7[c]
	100.0	100.0	100.0	15.7[c]

a The D_2:hydrocarbon ratio was 4:1 in this experiment.

b M_x is the mean number of deuterium atoms in the pseudo- parent ions from exchanged molecules.

c These percentages probably include some primary deuterium atoms from isomerised products.

d Some 7% of the total deuterium was present as secondary or tertiary atoms in isomerised products.

and TMP, with the deuterium distribution for the latter molecule being in good agreement with the calculated distribution expected for 15 exchangeable hydrogens, table 6.6. With TMP at 456K, however, there appears to be a small contribution from other processes; either from multiple exchange or from isomerisation. Previous results with this hydrocarbon using Pd films had indicated that some cyclisation to 1,1,3,3-tetramethylcyclopentane and isomerisation to 2,2,4-trimethylhexane occurred at 468K[7]. Nevertheless it is clear that the dominant mechanism with DMP, TMB and TMP over supported palladium is the reversible formation of adsorbed alkyl intermediates and that little dissociation to either $\alpha\alpha$- or $\alpha\gamma$-adsorbed species takes place. This behaviour is in marked contrast to the very extensive multiple exchange found with the linear and branched hydrocarbons described in the previous chapter where the ability to lose hydrogens to form alkene intermediates allows multiple exchange to occur by the $\alpha\beta$-process. The hydrocarbons with the quaternary carbon atom do not have this facility.

The kinetically well behaved exchange reactions observed with palladium, figure 6.4, and the identical rates and common activation energy for all three reactants, figure 6.6, may be a consequence of the fact that stepwise exchange is effectively the sole process occurring over palladium in the temperature range used. The carbon-hydrogen bond strengths in the methyl groups

attached to the quaternary carbon atoms are presumably similar for all the reactants and the minor differences in the nature of the rest of the molecules have no influence on the reaction over palladium.

6.5.2 Rhodium

This metal as shown by the mass spectrometric distributions for DMP, tables 6.1 and 6.8, demonstrates the greatest contributions from multiple exchange. Further confirmation of this is found from analysis of the nmr spectrum in figure 6.3(b); see table 6.4. The large presence of deuterium in $-CH_2D$ however shows that even at 450K stepwise exchange, i.e. process I, is still an important component of the exchange mechanism. The type of multiple exchange which occurs to an appreciable extent is process II, i.e. multiple exchange in a single methyl group leading to D_2- and D_3-ions and the formation of the groupings $-CHD_2$ and $-CD_3$, peaks B and D in figure 6.3(b). At this high temperature there is also some contribution from process III, involving $\alpha\gamma$-diadsorbed intermediates. This leads to products with deuterium atoms in two or more methyl groups and is clearly observed in the ^2D nmr spectrum where sufficient multiple exchange has occurred to separate $-CHD_2$ and $-CD_3$ groups with several γ-neighbours, peaks C and E, respectively, in figure 6.3(b).

As rhodium promoted the exchange of DMP by all three

processes pressure dependence experiments were carried out to determine the influence of deuterium pressure on the contributions of the separate mechanisms. Information was abstracted from the nmr spectra of the percentage of groups present with gamma interactions and these were fully attributed to process III. The amount of exchange by process II was deduced from the percentages of $-CHD_2$ and $-CD_3$ resonances, and exchange by process I was assumed to be the percentage in the $-CH_2D$ resonance. The relative amounts so calculated are given in table 6.10 and were used to apportion the calculated initial rate to the respective processes. The calculated pressure dependences are given in the last row of table 6.10. These data suggest that the overall rate of exchange was inhibited by deuterium - presumably because it was more strongly adsorbed than the hydrocarbon. The additional negative pressure dependence found for process III may arise because the mechanism involves a more dissociated form of the hydrocarbon or possibly an additional surface site.

The mass spectrometric results in table 6.7 and the nmr analyses in table 6.9 and figures 6.8 and 6.10 show that multiple exchange also occurred with TMB and TMP. Process II, already shown to be an important component of the exchange process of DMP was also important with TMP but less so with TMB.

The differences between the three reactants in regard to the extent and contribution of more general multiple

Table 6.10

Influence of Deuterium Pressure on the Exchange of 2,2-Dimethylpropane (4.4 k Pa) on Rhodium at 450K

Experiment	Deuterium Pressure (kPa)	Total Rate 10^{-2}r/molecule $^{S-1}$ (Rh atom)$^{-1}$	Percentage Contribution of Mechanisms		
			I	II	III
RHDMP1	8.8	16.3	30	12	58
RHDMP2	17.5	8.8	38	12	50
RHDMP3	35.0	6.8	46	17	37
	Pressure Dependence	-0.5	-0.3	-0.3	-1.0

exchange processes over rhodium are demonstrated most clearly in the values in figure 6.7 of M, which are higher for TMB than for DMP or TMP. The interest lies in the extent to which ions with 10 or more deuterium atoms are observed in the early stages of reaction with TMB or TMP. Such ions provide evidence for initial products resulting from a multiple exchange process capable of exchanging both ends of the molecules. A mechanism involving $\alpha\delta$-diadsorbed intermediates is necessary to give this kind of exchange with TMB, see scheme 6.1. Two mechanisms might operate with TMP, i.e. either (i) multiple exchange via $\alpha\varepsilon$-diadsorbed species, or (ii) propagation of the exchange over the whole molecule via $\alpha\gamma$-species involving the central $-CH_2-$ group, see scheme 6.2. The latter can be ruled out since no evidence for deuterium atoms in the methylene group was found in the nmr spectra of the products. Bearing in mind possible contributions from multiply-exchanged isomerisation products of TMP it is believed that insufficient $D_{10}-$ or higher ions are observed to indicate that $\alpha\varepsilon$-diadsorbed species contributes significantly to the exchange of this molecule over rhodium. In other words, TMP and DMP show similar extents of general multiple exchange involving $\alpha\gamma$-intermediates which can lead to complete exchange for DMP and exchange limited to the three methyl groups at one end only for TMP. The situation is different with TMB which gives initially more ions in the range from D_{10} to

D_{15} than from D_4 to D_9. Obviously the exchange process can propagate over all six methyl groups in the molecule which requires a mechanism involving interconversion between alkyl and $\alpha\delta$-diadsorbed intermediates, see scheme 6.1. This form of exchange mechanism is designated process IV. The maxima in the distributions of the ions at D_9, D_{12} and D_{15} which can be seen in the results for experiment RHTMB2 in table 6.7, provide evidence of another aspect of process IV. There must be some means which assists the completion of the exchange of the methyl groups involved in the $\alpha\delta$-bonding to the catalyst surface. A likely explanation of this behaviour is that $\alpha\delta$-intermediates can interconvert with$\alpha\alpha\delta$-adsorbed or more highly dissociated forms. The shape of the distributions of ions suggests that rhodium forms $\alpha\delta$-adsorbed species more readily than $\alpha\gamma$-adsorbed species with TMB. The nmr traces in figures 6.8 and 6.10 show that TMB generates more of the $-CD_3$ grouping with high exchange in the remainder of the molecule than either DMP or TMP. This is confirmed in the quantitative results given in table 6.9. All these results combine to demonstrate that with TMB over rhodium the main mechanisms of exchange are stepwise exchange and process IV with only a minor contribution from process II. In contrast with DMP and TMP stepwise exchange and processes II and III occur together with some isomerisation of TMP.

Self-poisoning of the exchange reactions appears to be

a characteristic of rhodium catalysts. As shown in figure 6.5 the influence of self-poisoning is greater with DMP and least with TMP. The explanation is probably due to the formation of highly dissociated adsorbed species which are more strongly adsorbed and less readily rehydrogenated. Such species may play an important role in hydrogenolysis which is known[8] to occur with DMP at 463K, i.e. only 40K above the highest temperature used in the present study with rhodium. Because of the variety of reaction mechanisms and possible complications at higher temperatures from self-poisoning of the exchange reactions over rhodium it is perhaps not surprising that the results shown in figure 6.6 for the metal show the greatest scatter.

6.5.3 Iridium

At 460K the results from DMP exchange, shown in tables 6.1 and 6.4, and figure 6.1, show that although there is still a significant amount of stepwise exchange there are small contributions from processes II and III with this metal. Process II, methyl group exchange, produces the identifiable groups $-CHD_2$ and $-CD_3$ in figure 6.1, and process III yielding exchange products greater than D_3 is the cause of the shifted $-CD_3$ group. This is due, as in rhodium, to several gamma interactions from multiply exchanged molecules. At the lower temperatures used for comparison of DMP exchange with TMB and TMP, however,

there was relatively little evidence for general multiple exchange, the dominant process with all three reactants being stepwise exchange with only a minor contribution from process II, as tables 6.7 and 6.9 indicate. General multiple exchange although just detectable appears to be more extensive with TMB, see table 6.7 and figure 6.7, than with the other reactants. Thus, as with rhodium, $\alpha\delta$-adsorbed intermediates may be formed more readily than $\alpha\gamma$-species but neither play a substantial part in the mechanism of exchange over this catalyst. This is in contrast to reported results of DMP exchange over silica-supported rhodium and iridium catalysts at 360K where as well as their activities being similar, the extents to which both metals promoted general multiple exchange were also the same[2]. The reason for the difference may, in part, be due to the small metal loading (i.e. 0.5% w/w) of the Ir/Al_2O_3 catalyst, with significant amounts of stepwise exchange taking place over the support as discussed in the preceeding chapter.

6.5.4 Platinum

Results in tables 6.1 and 6.6 and figure 6.3 show that multiple exchange of DMP occurs over this metal with process II being more important than process III. The character of the latter process however is not the same on platinum as on rhodium. Table 6.1 shows that in the exchanged products over platinum the amounts of ions with

4 or more deuterium atoms decrease with increasing deuterium content. This is also the case with the longer hydrocarbons TMB and TMP, table 6.6. As the average number of deuterium atoms acquired by any of the hydrocarbons undergoing $\alpha\gamma$-type exchange over platinum was not as great as with rhodium, this implies that the number of alkyl to $\alpha\gamma$-adsorbed interconversions before an exchanged molecule desorbs is not as large on platinum as on rhodium. The M values for all three reactants are similar over platinum, table 6.6, and the extent of multiple exchange depends mainly on the temperature of reaction and not on the nature of the hydrocarbon. The spectra in figure 6.9 show that the nmr traces for fairly extensively exchanged TMB and TMP are similar and the resonances for $-CHD_2$ and $-CD_3$ groupings are broadened but not resolved. Thus the average number of gamma isotopic shifts is insufficient to give rise to separate resonances as was found with rhodium. This is clearly seen in figure 6.3 for DMP exchanged to similar extents over the two metals. At 423K, TMB and TMP both give about 0.8% of ions in the range from D_{10} to D_{14} at 15% conversion, as shown in table 6.6, but this does not amount to significant evidence for a contribution from $\alpha\delta$- or $\alpha\varepsilon$-adsorbed intermediates since 1% of the molecule will have undergone repeated reaction at this conversion.

6.5.5 Reactions other than Exchange and Comparative Rates of Exchange of the Metals.

Previous studies with TMP on sintered films of iridium, palladium, platinum and rhodium[7] had shown that appreciable cyclisation and isomerisation of this molecule occurred by $\alpha\varepsilon$-diadsorbed species. The sintering of the films had the effect of reducing the rate of the exchange reactions so that the processes of isomerisation and dehydrocyclisation could be studied without complications from exchange. Although the temperatures used in this study were only slightly lower than those used over the sintered metallic films, the supported catalysts gave only exchange without the complication of other reactions, except in the case of rhodium. The presence of some 6-7% of the total deuterium in the products from the TMP-rhodium system in nmr peaks with δ = 1.45 p.p.m. provided evidence of isomerisation but there was insufficient data to identify the products. Finlayson *et al*[7] reported that 2,2,5-trimethylhexane was the major product over sintered rhodium at 573K and obtained evidence for a D_{11} ion (m/e = 124) in the relevant mass spectrum. The present results for the reaction of TMP over supported rhodium at 393K show small maxima for the D_8 and D_{11} ions, table 6.7, which may have resulted from isomerised products. Since the peaks around δ = 1.45 p.p.m. would have represented secondary or tertiary deuterium atoms in the isomerised products it is probable

that primary deuterium atoms in these products contributed to the same region of the nmr spectrum as the primary atoms in exchanged TMP, as suggested in table 6.9.

No evidence for isomerisation of DMP or TMB was found in the current study over rhodium or the other three supported metals and it is pertinent to consider why only TMP should react in this way. The results reported by Finalyson *et al*[7] provide a possible explanation. The main type of isomerisation observed with TMP over rhodium films was the formation of 2,2,5-trimethylhexane and the mechanism was thought to involve a 1,2-neopentyl shift of an adsorbed alkyl species. This type of reaction cannot occur with the smaller molecules DMP and TMB which would have to isomerise by a 1,2-methyl shift : a reaction which occurs less readily on rhodium films than the neopentyl shift[7].

The results in figure 6.6 permit a comparison of the four metals for exchange of the three hydrocarbons. The ratios of the activities at 400K, ignoring any differences, in the degree of dispersion are 260:120:60:1 for Pt:Ir:Rh:Pd. These ratios are in broad agreement with results from earlier studies with DMP[4,5].

6.6 CONCLUSIONS

The relative importance of the various mechanisms and the role and reactivity of the hydrocarbon intermediates may be influenced by a number of factors such as the

crystal faces exposed, dispersion, interactions with the support and the source of the labelling deuterium. The effect of some of these factors was shown by Long *et al*[9] who obtained results using proton nmr on the relative exchange of primary, secondary and tertiary hydrogens for various carbon/metal film systems. Perhaps the most striking feature, however, is the relatively small variation in behaviour of any given metal in exchange reactions with the form in which it is used[10-12]. For a range of hydrocarbons each metal appears to give its own characteristic product distributions which are influenced to a lesser degree by the other factors listed above. The differences between the metals are clear and easy to discern if a range of reactants are used as in the present work.

It is unlikely that geometrical considerations can account for the large variations in the behaviour of the four metals used. All form face-centred cubic crystals and the metal-metal spacings have a small range; from 269 pm(Rh) to 275 pm(Pd). The main conclusions about the catalytic behaviour for the hydrocarbon reactions can be summarised briefly.

Iridium. The results over this metal were dominated by the stepwise exchange of primary hydrogens on the alumina support - especially with linear and branched hydrocarbons. At the higher temperatures used for the hydrocarbons containing quaternary carbons limited

multiple exchange mainly by process II but with some general multiple exchange was possible. The latter was more extensive with TMB indicating the $\alpha\delta$-diadsorbed species may be formed more readily than $\alpha\gamma$-species.

Palladium. This metal proved to be the most effective for multiple exchange of any hydrocarbon for which an $\alpha\beta$-process was possible. However, it demonstrated the lowest activity for promoting the formation of $\alpha\alpha$- or $\alpha\gamma$-intermediates even at the higher temperatures used for the more branched hydrocarbons.

Rhodium. This metal was the most versatile of the four metals investigated and promoted the greatest variety of intermediates and reaction mechanisms, even for the simpler molecules. With the linear and branched hydrocarbons exchange occurred via $\alpha\gamma$-intermediates as well as via the $\alpha\beta$-process. With the hydrocarbons containing quaternary carbons process II, $\alpha\alpha$-exchange, also proved to be an important aspect of the exchange process. With TMB, however, process IV, the formation of $\alpha\delta$-diadsorbed intermediates, proved to be the main mechanism for general multiple exchange. There was no significant evidence for $\alpha\varepsilon$-diadsorbed species with TMP.

Platinum. This metal as well as having a tendency to promote stepwise exchange showed properties akin to palladium with respect to the linear and branched hydrocarbon molecules. With the more branched hydrocarbons the main process of exchange were types I and

II with some contribution from $\alpha\gamma$-exchange, although this was not as great as over rhodium.

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CHAPTER 7

MECHANISTIC STUDIES OF HYDROCARBON EXCHANGE REACTIONS OVER SUPPORTED METAL CATALYSTS

III Exchange and Addition of Deuterium to 2-Methylpropene

7.1 INTRODUCTION

Although the results from deuterium addition and exchange of alkenes have previously been alluded to briefly in chapter 2, the information below is a more comprehensive study of the literature on these reactions. It can be subdivided into three parts: (i) early studies on metal films and supported metals relying on mass spectrometry for elucidation of the amounts of formed deuteroalkanes and deuteroalkenes; (ii) more recent studies where the use of microwave spectroscopy has been helpful in determining the location of the deuterium atoms in the exchanged alkenes; and (iii) studies in an aqueous medium using electrodes or suspended particles as the catalysts in the presence of deuterated acids and/or deuterium gas and reliance on mass spectrometry for estimation of the deuterium content of the formed alkenes.

7.1.1

The early investigations of the reactions of alkenes with deuterium over metals have been reviewed[1]. An important component of the mechanistic aspects of these

reactions has been the reversible formation of adsorbed alkyl radicals on the catalyst surface, the so-called 'half-hydrogenated state' as defined by Horiuti and Polyani[2]. Reactions such as exchange of the alkene with deuterium and isomerisation of alkenes can be explained satisfactorily in many cases by these alkyl reversal processes that are classified as associative mechanisms. Some success was achieved in a quantitative interpretation of the amounts of the various isotopic ethenes and ethanes formed from the reaction of C_2H_4 and D_2 on evaporated metal films[3] in terms of the relative rates of the various reactions of adsorbed ethene and adsorbed ethyl species and the same approach has been extended to results over alumina-supported platinum and iridium catalysts[4]. This type of analysis however became complex as the number of carbon atoms in the alkene increased, thus the results for larger alkenes were treated in a more qualitative nature. For example as the results for propene were similar to those of ethene over palladium the formation of a π-allyl species was not considered. Indeed the evidence for participation of such an intermediate over the full range of metals studied was poor. In conclusion Bond and Wells[1] stated that the Group VIII metals fell into two broad groups. Iron, nickel and palladium were active in isomerisation and alkene exchange whereas platinum and iridium were found to be almost inactive for these reactions. The other metals ruthenium, rhodium and osmium

occupied an intermediate position.

7.1.2

By application of microwave spectroscopy progress has been made in the identification of reaction intermediates during the reactions of propene and but-1-ene with deuterium over metals, firstly by Kozo Hirota[5] and subsequently by F.G. Gault[6].

Preliminary reports for Pd and Ni powders[7,8] where propene was exchanged with D_2O and D_2 gas suggested that the central hydrogen atom of the alkene was the most susceptible to exchange on Ni whereas with Pd all the hydrogens showed nearly equal activities. Formation of a dissociated intermediate as well as the half-hydrogenated alkyl was thought to exist during the addition reaction. A dissociated state of propene was proposed to exist on Pt black[9] which was not observed on the previous two metals. This species was favoured to explain the greater amount of exchange of the *trans*-vinyl hydrogen, among the six hydrogen atoms there was also a considerable amount of deuterium in the central position. By extending their research to Rh and Cu[10] and comparing the results previously found for Ni, Pd and Pt they were able to ascertain that the adsorbed species of propene were drastically different according to the metal, thus (i) Ni and Cu promoted exchange of the central hydrogen; (ii) all the hydrogens were equally exchangeable on Pd and

(iii) with Pt exchange of the *trans*-vinyl position was favoured over the *cis*-position. A general reaction scheme was proposed where a dissociative intermediate was formed, but it was not considered to be involved in the addition reaction which occurred via alkyl intermediates, but it was thought that dissociated species would occur at low hydrogen pressures. The dissociative states of chemisorbed propene on Ni, Pd, Pt, and Rh were further examined by the investigation of propene-3-d_1[11] but little difference in the metals was found apart from the finding that a π-allyl intermediate was produced more readily on Rh than on Pt or Pd.

Initial work by Gault and his co-workers[12] using only mass spectrometry and gas chromatography to study the exchange of alkenes in the presence of C_3D_6 on Fe films gave results which only exchange of the vinylic hydrogen could adequately explain. In the case of ethene all four hydrogens were exchanged, and for propene only the three vinylic hydrogens were replaced by deuterium, but as the alkyl substituent of the 2-alkene increased the amounts of multiple exchange also increased and the differentiation of one vinylic hydrogen became more pronounced. The authors suggested that the vinylic hydrogen atom which is more rapidly exchanged than the other two is the internal vinylic hydrogen. Later work involving microwave spectroscopy[6] allowed determination of the exchanged products from n-butene exchange and isomerisation with

C_3D_6 showed that the main product was d_1-but-1-ene with increasing amounts of extensively exchanged molecules up to d_7-but-1-ene, and microwave spectroscopy showed deuterium in the singly-exchanged molecule to be located mainly on C_3(~ 60%) and C_1(~ 40%) with the 1-*trans*-position largely predominant over the 1-*cis*-position. These results forced the conclusion that the associative Horiuti-Polyani mechanism did not operate for but-1-ene exchange and the preferred mechanism proceeded by dissociative adsorption. The authors believed that exchange by vinylic or allylic mechanism operated concurrently. The allylic type mechanism explained the formation of 3-d_1-but-1-ene and the vinylic species accounted for the disproportionate amounts of *cis*-1-d_1-but-1-ene and *trans*-1-d_1-but-1-ene.

Similar studies on Ni films[13] showed that in all the experiments the most abundant product was 2-d_1-but-1-ene. In the presence of C_3D_6 at 273K *trans*-1-d_1-but-1-ene predominated over the *cis*-d_1-product, whereas in the presence of deuterium gas at 189K the differences in these two isomers was small. Again, as was the case for Fe, a dissociative mechanism involving the unequal breaking of the two terminal C-H bonds was also taking place, but the authors do not exclude alkene-alkyl reversal. Participation of the Horiuti-Polyeni mechanism was evident in the presence of D_2 at 189K which suggested that vinylic-type dissociative adsorption was a more activated

process than alkene-alkyl reversal. Although the fast incorporation of deuterium in C_2 could be explained by an associative mechanism involving a 1-butyl intermediate "indirect" reasoning leads the authors to suggest that the 2-d_1-but-1-ene is mainly formed from a σ-vinylic adsorbed species.

Results found for nickel supported on silica[14] parallelled those found for Ni films[13], thus the dissociative mechanism with preferential formation of a 2-butyenyl radical was again proposed. On supported Pd, however, 90% of the deuterium was found to be localised on C_1 with no significant distinction between the two vinylic hydrogens, these results are quite different from those realised earlier with Pd films.

Latterly[15], addition and exchange of deuterium on a 10% w/w nickel on pumice catalyst with substituted cyclopentenes and but-1-ene confirmed the authors' thoughts that in the reactions of alkenes with deuterium the Horiuti-Polyani mechanism is not the only one operating. Their results for but-1-ene showed addition to be approximately twice as fast as exchange and at all temperatures the deuterium in d_1-but-1-ene was localised on C_2. This preference for exchange in the C_2 position was explained by the formation of a secondary vinylic species which is more reactive than primary ones. The similarity between Ni and Fe was underlined, i.e. preference for exchange in C_2 position and a similar

behaviour for the isomerisation of the but-1-ene molecules.

More recently the results from microwave spectroscopy to study the mechanisms of deuterium addition and exchange of propene over metal-supported catalysts have been reported[16-18]. It is demonstrated within these reports that dissociative and associative mechanisms should not be adopted at the same time, the importance of either depending on the presence of hydrogen. Without hydrogen, light propene, C_3H_6, exchanges with C_3D_6 and three intermediates are formed, 1-propenyl, 2-propenyl and σ-allyl, the importance of each differing with the catalyst used. The results for Ni/SiO_2 confirmed the earlier findings of Hirota[5] that over this metal the hydrogen in C_2 was more readily exchanged. Previous results with Pd had indicated that all the hydrogens were equally susceptible for exchange, at the low temperatures used in the present work, 249K, the hydrogens on C_1 followed by those on C_3 proved to be more exchangeable. They dismissed the formation of a π-allylic species because of the inability at low temperatures for there to be any extensively exchanged propene in the C_3H_6-C_3D_6 reaction. Over Pt, all the hydrogens seemed to be equally exchangeable.

In the presence of hydrogen the intermediates involved in the exchange of propene were 1-propyl and 2-propyl and the hydrogen in this case which proved to be more

susceptible to exchange were those on C_2 for Ni, Cu, Ag and Au and those on C_1 for both Pt and Pd. Double bond movement was considered to be an intramolecular process where a rapid shift of hydrogen from C_1 to C_3 occurred. For all the metals, apart from Pt, exchange proved to be faster than the addition reaction, for Pt addition was twice as fast as exchange.

7.1.3

The addition of deuterium to propene and 2-methylpropene was studied over Pt/graphite suspended in D_2SO_4[19,20] with the resultant alkanes being analysed mass spectrometrically. The deuterium distributions in each alkane **were** found to exist in two segments. With propene, there was a minimum at d_6-propene whereas for 2-methylpropene the two segments were separated by an exceptionally small amount of d_5-2-methylpropane. This represented the number of exchangeable hydrogens in the two alkenes being 5 and 4 respectively. The difference in the amounts of deuterium could only be explained by assuming that hydrogen atoms at the vinylic position of the reactants are exchangeable.

$$\text{i.e. } CH_2{=}CHCH_3 \xrightarrow{D(a)} CD_3CD_2CH_3$$

$$CH_2{=}C(CH_3)_2 \xrightarrow{D(a)} CD_3CD(CH_3)_2$$

In the case of 3,3-dimethylbut-1-ene only one exchanged segment appeared in the deuterium position

$$CH_2=CH-C(CH_3)_3 \xrightarrow{D(a)} CD_3CD_2C(CH_3)_3$$

thus the highly deuterated species observed with propene and 2-methylpropene were obtained by migration of the double bond. To explain the preferential exchange of the vinylic positions the authors preferred restricted rotation of the half-hydrogenated species, *iso*-propyl and *tert*-butyl intermediates, having previously dismissed the formation of adsorbed vinylic species because unreacted propene did not contain any deuterium and self-exchange nor hydrogenation occurred when a mixture of CH_2CH_2 and CD_2CD_2 was contacted with their catalyst.

Thus from the foregoing little work has been done on the reactions of 2-methylpropene. This was felt to be a less complicated molecule to study than propene because it has only a single pair of identical vinylic hydrogens compared to the three distinguishable types of vinyl hydrogens which propene possesses and it seemed that a more satisfactory investigation of the relative contributions of associative and dissociative processes could be made with this molecule. An early investigation on a nickel catalyst[21] showed that the main product was d_2-alkane in contrast to the spread of isotopic products obtained with other alkenes. Hirota *et al*[22] used microwave spectroscopy to analyse the alkenes and alkanes obtained from 2-methylpropene reactions on various

supported metal catalysts and related organometallic complexes. They concluded that the main mechanisms of exchange were alkyl-reversal with some contributions from π-allyl species but they found no evidence of a role for vinyl species. Microwave spectroscopy, although it is a sensitive technique capable of examining small samples, is not ideally suited for determining the position of deuterium atoms in 2-methylpropene because of the complexity of the rotational spectra, and it is even less satisfactory with 2-methylpropane which has a lower dipole moment. Deuterium nmr spectroscopy on the other hand, provides a very useful technique for obtaining detailed information on the distribution and grouping of deuterium atoms in the products from the reactions of 2-methylpropene and deuterium as shown by recent work with various oxide catalysts[23].

The main objective of the work described in the present chapter was to use the technique of deuterium nmr spectroscopy combined with mass spectrometry and gas chromatography to examine the products from the reaction of 2-methylpropene with deuterium on a range of supported metal catalysts. Again the emphasis of the work was directed towards the determination in some detail of the distributions of deuterium atoms in the products and not on the evaluation of rates or other kinetic parameters. It was hoped that such information might provide a clear indication of the relevant roles of associative and

dissociative mechanisms for the reactions of 2-methylpropene on the metals and the contributions of vinyl or allyl species in the dissociative processes. Similarly an experiment with propene was carried out in order for comparisons to be made with previously published data[16,17].

7.2 EXPERIMENTAL

These studies were carried out on the recirculation apparatus (line 3) previously described in section 3.2.1, which had the facilities for both mass spectrometry and gas chromatography, the conditions for the latter technique having been given in 3.2.3. The pressure of alkene used was 2.7 kPa, which corresponded to a charge of 2.3×10^{20} molecules and the normal ratio of deuterium to hydrocarbon was 5:1. Some experiments were carried out with a 1:1 mixture and the balance was made up with helium which was purified by passing it through an oxygen trap and a molecular sieve held at liquid nitrogen temperature.

The catalysts used were the same as those described in section 5.2, except that the Pt/Nb_2O_5 sample used in the studies described in chapter 4 was used instead of the silica-supported platinum.

Samples for analysis by nmr spectroscopy were obtained by condensing the hydrocarbons in a trap held at liquid nitrogen temperature after about 15 to 20% of alkane had been formed and subsequently distilling them into an nmr

sample tube as described elsewhere, section 3.3. Mass spectrometric analyses were also made on the reaction mixture after the required amount of addition had occurred and the catalyst had been isolated. These were obtained by using 15 eV electrons to ionise the molecules. At this voltage calibration experiments showed that the sensitivity for the alkene parent ion (m/e = 56) was 18 times that for the alkane parent ion (m/e = 58). When the exchange of the alkene was not extensive, peaks from m/e = 60 upwards were assigned to isotopic alkanes and the usual correction made for naturally occurring isotopes and fragmentation. In this way the relative amounts of d_2- and more highly deuterated alkanes were determined. The residual peaks from m/e = 56 to m/e = 59 were used to estimate the relative amounts of the d_0- to d_3-alkenes. In some of the experiments which were carried out after the sensitivity of the ion multiplier in the collector of the mass spectrometer had been improved, it was possible to obtain kinetic analyses for the exchange of the alkene by using an ionising voltage of 9 eV. With this voltage the contribution from the alkanes was negligible. The deuterium distributions in the propene and propane were measured at 10 eV where, due to a change in mass spectrometer, the propene parent ion (m/e = 44) was only 3 times more sensitive than the propane parent ion. This value was independent of the ionising voltage used. At 10 eV both hydrocarbons also gave substantial amounts of

fragmentation ions, thus to fully evaluate the deuterium distributions the information about the relative amounts of D in the alkene and alkane from the nmr spectra as well as the quantities of each from the gas chromatographic data was utilised. This gave a ratio for the amount of D that should be in the hydrocarbons and with the assumptions that the peak at m/e = 46 was due to d_2-alkane and the amounts of d_1/d_0 would be approximately equal to d_4/d_3 the deuterium distributions in the propene and propane were estimated.

7.3 RESULTS

7.3.1 Nmr Analyses

The analyses of the 2-methylpropene and propene nmr spectra were made following procedures previously outlined[23,24]. For 2-methylpropene the groups CHD= and CD_2= gave resonances at δ = 4.689 and 4.674 p.p.m. corresponding to an α-shift of -15 p.p.b. caused by the presence of the second D atom. The resonance from $-CH_2D$ occurred at δ = 1.72 p.p.m. and the corresponding α-shift for $-CHD_2$ was -19.5 p.p.b. The spectra for the alkanes formed were similar to those given previously in section 5.4 and by Bird *et al*[23]. The spectrum covering the region of the methyl groups of the alkene and the tertiary deuterium atom of the alkane is shown in figure 7.1. The large peak at δ = 1.682 p.p.m. corresponds mainly to the molecule $CD(CH_2D)(CH_3)_2$ in which the tertiary D atom is

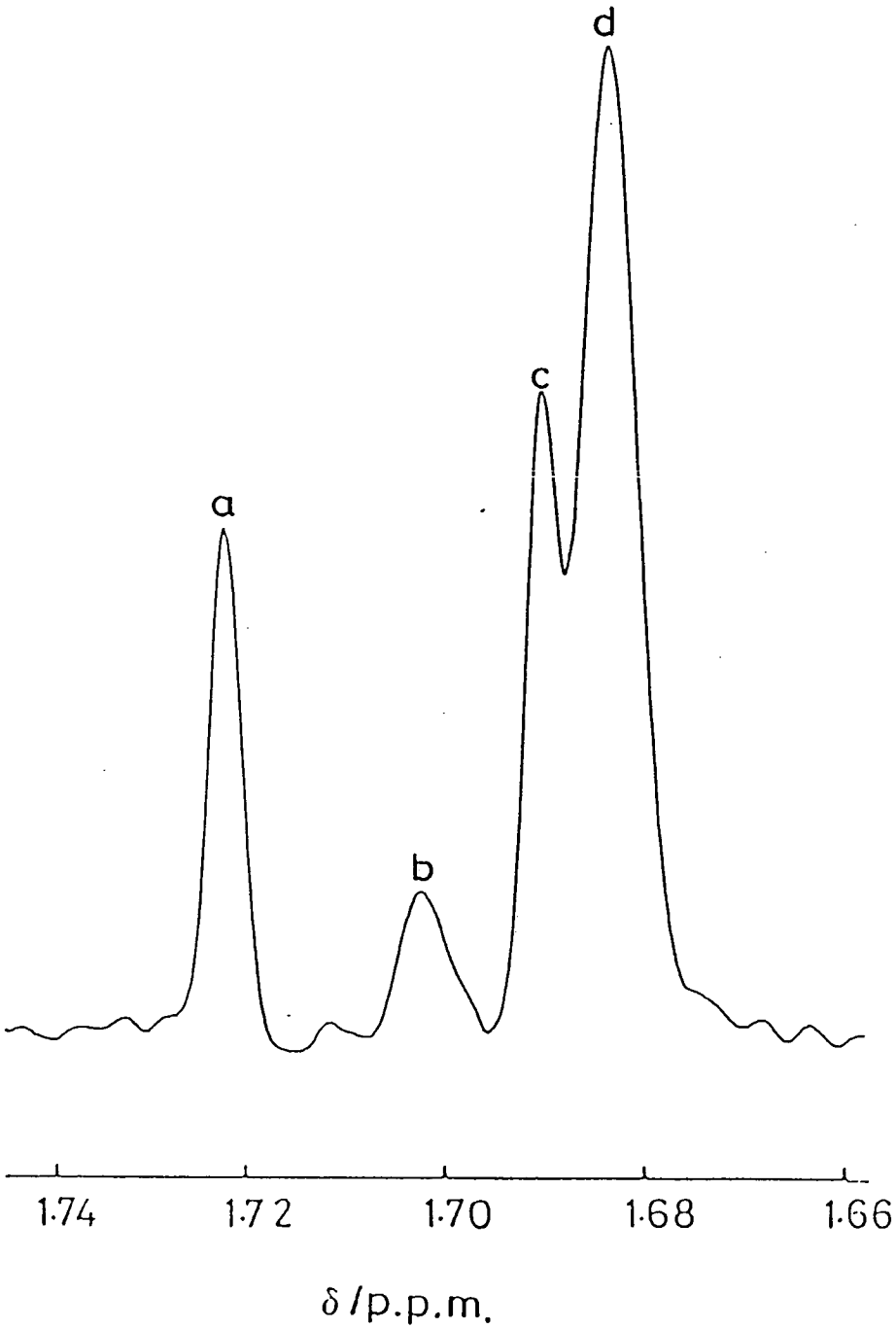


Figure 7.1 Part of the nmr spectrum from experiment Pt3(LTR). The resonances a and b result from the methyl groups $-CH_2D$ and $-CHD_2$ of the alkene; the resonances c and d result from the tertiary D atom of 2-methylpropane as $CD(CH_3)_3$ and $CD(CH_2D)(CH_3)_2$ respectively.

subject to a β-shift of -7 p.p.b. as a result of the D atom in one of the methyl groups. The smaller peak at δ = 1.689 is due to tertiary D in $CD(CH_3)_3$. In the experiment shown in figure 7.1 the 2-methylpropene was not extensively exchanged and so the contribution of a peak due to $-CD_3$ in the alkene which should occur at δ = 1.683 p.p.m. is likely to be small and will only amount to a low percentage of the large resonance at this position. In contrast, the spectrum shown in figure 7.2 for a sample after reaction over palladium has a broad resonance at δ = 1.683 p.p.m. which included contributions from $-CD_3$ in the alkene and tertiary D in the alkane and a direct estimation of the individual contribution was not possible. Figure 7.3 shows the sequence of resonances found for primary D atoms in the alkane in the products from two experiments. The peaks corresponding to - CH_2D, $-CHD_2$, and $-CD_3$ are well separated, as previously shown in section 5.4, because the α-shifts are about -21 p.p.b. The two components of each of these peaks, depending on whether the tertiary atom was H or D, are obvious in every case, but sometimes only poorly resolved because the β-shift is about -8 p.p.b. Even where this was incomplete, it was still possible to estimate what fraction of the molecules contained a D atom in the tertiary position from these spectra.

The nmr analyses obtained for all the 2-methylpropene experiments together with information on weight of

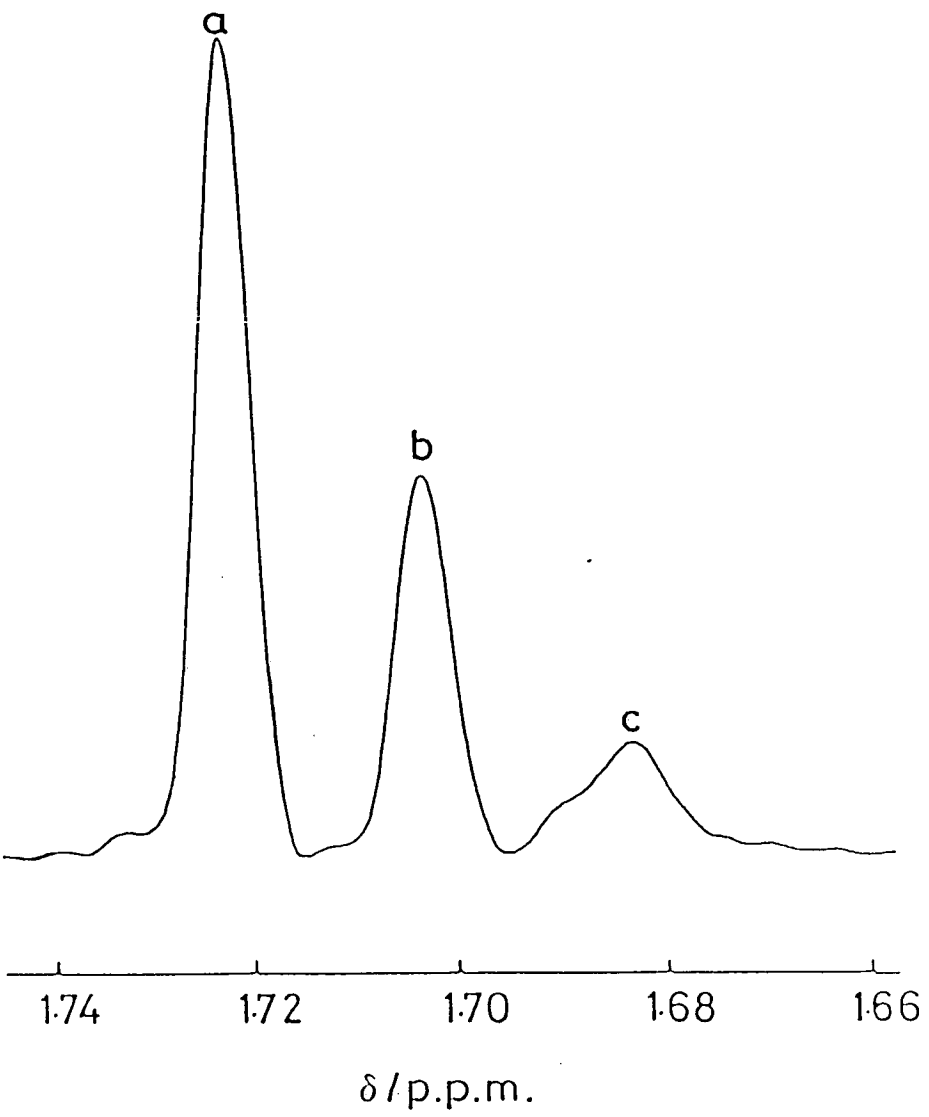


Figure 7.2 Part of the nmr spectrum from experiment Pd1 covering the same region as in figure 7.1. The resonances a and b result from the methyl groups $-CH_2D$ and $-CHD_2$ of the alkene. The small broad resonance c includes contributions from the $-CD_3$ group in the alkene and the tertiary D atom in the alkane.

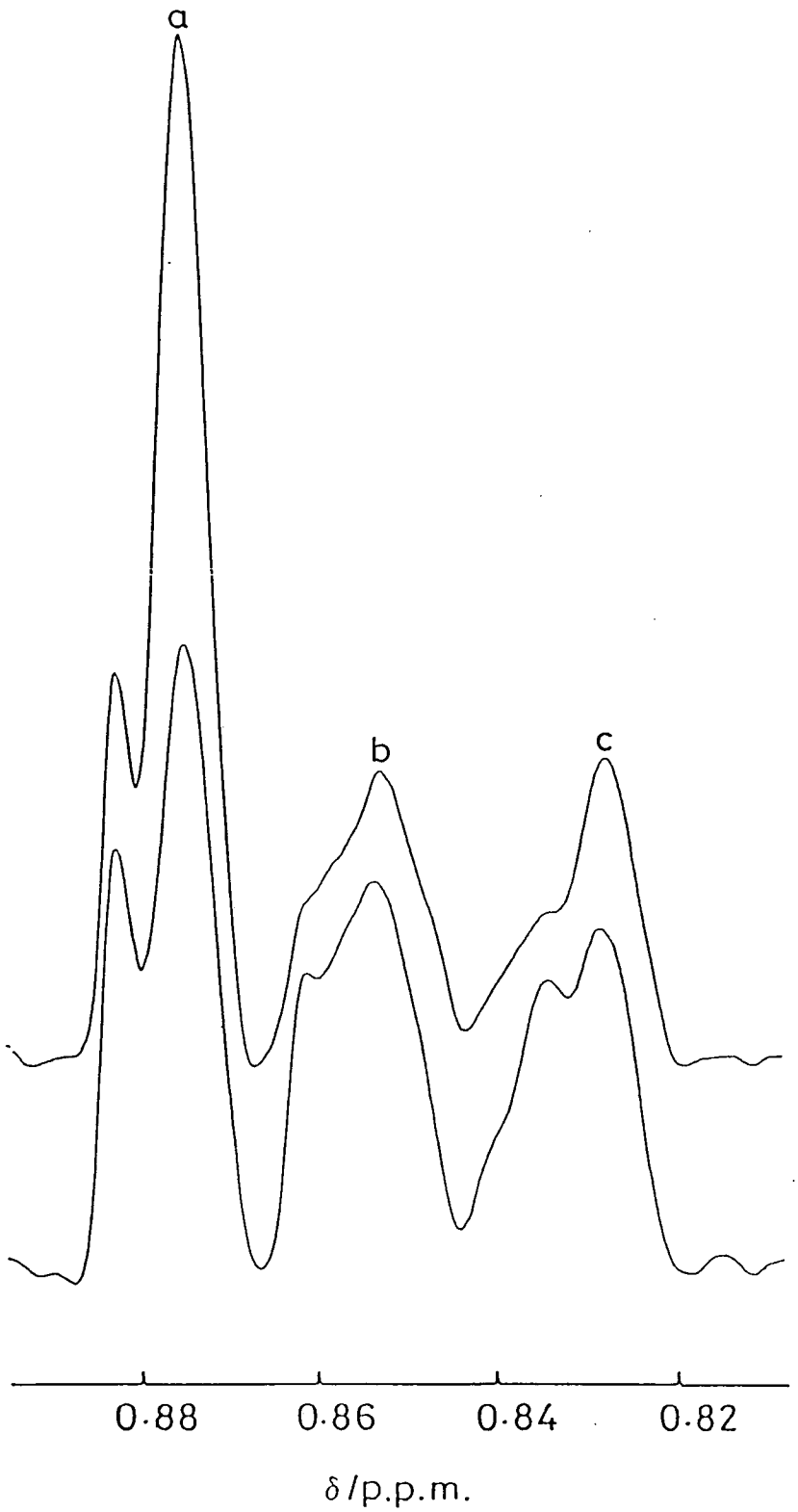


Figure 7.3 The nmr spectra for the primary D atoms in 2-methylpropane formed in the experiments Pt3(HTR), upper curve, and Rh2, lower curve. Peak a corresponds to the groupings $CHCH_2D$ and $CDCH_2D$, b to $CHCHD_2$ and $CDCHD_2$ and c to $CHCD_3$ and $CDCD_3$.

Table 7.1

Experimental Details and NMR Analyses of the Distribution of Deuterium in 2-Methylpropene and 2-Methylpropane

		Pt1(LTR)	Pt2(LTR)[a]	Pt3(LTR)	Pt4(HTR)	Rh1	Rh2	Rh3	Ir1	Pd1
cat. wt/mg		54	66	8.1	115	29	6.1	8.3	78	248
time/min		23	170	43	150	30	7	8	10	41
T/K		233	235	295	295	205	235	235	235	233
alkane %		13.9	17.0	18.3	20.8	18.2	20.9	99.6	23.1	19.2
D in alkene										
=CHD		5.4	5.1	4.2	7.9	2.9	2.2	-	-	15.1
$=CD_2$		-	1.0	1.4	1.3	1.0	0.8	-	-	3.8
$-CH_2D$		3.7	6.7	6.7	13.3	3.1	2.2	-	-	36.4
$-CHD_2$		-	1.2	2.7	2.6	-	0.8	-	-	17.9
$-CD_3$		-	-	-	-	-	-	-	-	9.0[c]
D in alkane										
3°D		39.2	37.5	29.5	25.6	29.4	27.2	24.1	47	9.0[c]
1°D[b]	$CHCH_2D$	-	(3)	5	(3)	6.2	6.3	(5.7)	-	6.5
	$CDCH_2D$	37.0	(32.6)	25.7	(23.3)	21.1	20	(18)	43	3.5
	$CHCHD_2$	-	6.9	(3)	(2.3)	17.6	(7.1)	(7.8)	-	3.0
	$CDCHD_2$	7.6		(10.1)	(10)		(14.6)	(18.2)	10	2.0
	$CHCD_3$	-	6.0	(3)	(2)	18.7	(7.5)	(9.9)	-	1.0
	$CDCD_3$	7.1		(8.7)	(8.7)		(11.3)	(16.3)	-	1.8
		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	

(a) Using a 1:1 ratio of D_2:hydrocarbon.

(b) Values in parenthesis represent approximate contributions from $CHCX_3$ and $CDCX_3$ groups.

(c) The combined percentage of D in these groups was 9.0.

catalyst, time and temperature of the reaction and percentage conversion to alkane are given in table 7.1.

The deuterium nmr spectra of the propanes formed over the supported platinum samples could be readily interpreted but the propene spectra were less readily so due to the small extents of alkene exchange. Figure 7.4 shows the secondary deuterium at δ = 1.302 p.p.m., the large peak corresponding to a single deuterium with a β neighbour in a methyl group, the two further resonances shifted -21.6 and -29.6 p.p.b. are caused by a second deuterium in the secondary position. The primary positions are shown on the right hand side of figure 7.4 where the main resonance, at δ = 0.886 p.p.m., is due to a primary deuterium with a secondary deuterium neighbour. The two split resonances are due to 2 and 3 D atoms in the methyl groups with the smaller peaks of the resonances caused by methyl groups without a β-neighbour. The presence of the shoulder on the main peak is an indication that some $-CH_2D$ methyl groups also do not have a β-neighbour. Although very little exchange occurred in the propene the relative amounts of D in the four hydrogen positions[24] could be determined, these results being given in table 7.2. Further information could be gained from the propene exchange in experiment Pt6 by measuring the peak heights for the individual species. The groupings of deuterium in the methylene showed that both of the methylene D atoms (*cis* and *trans*) had a 28% chance of

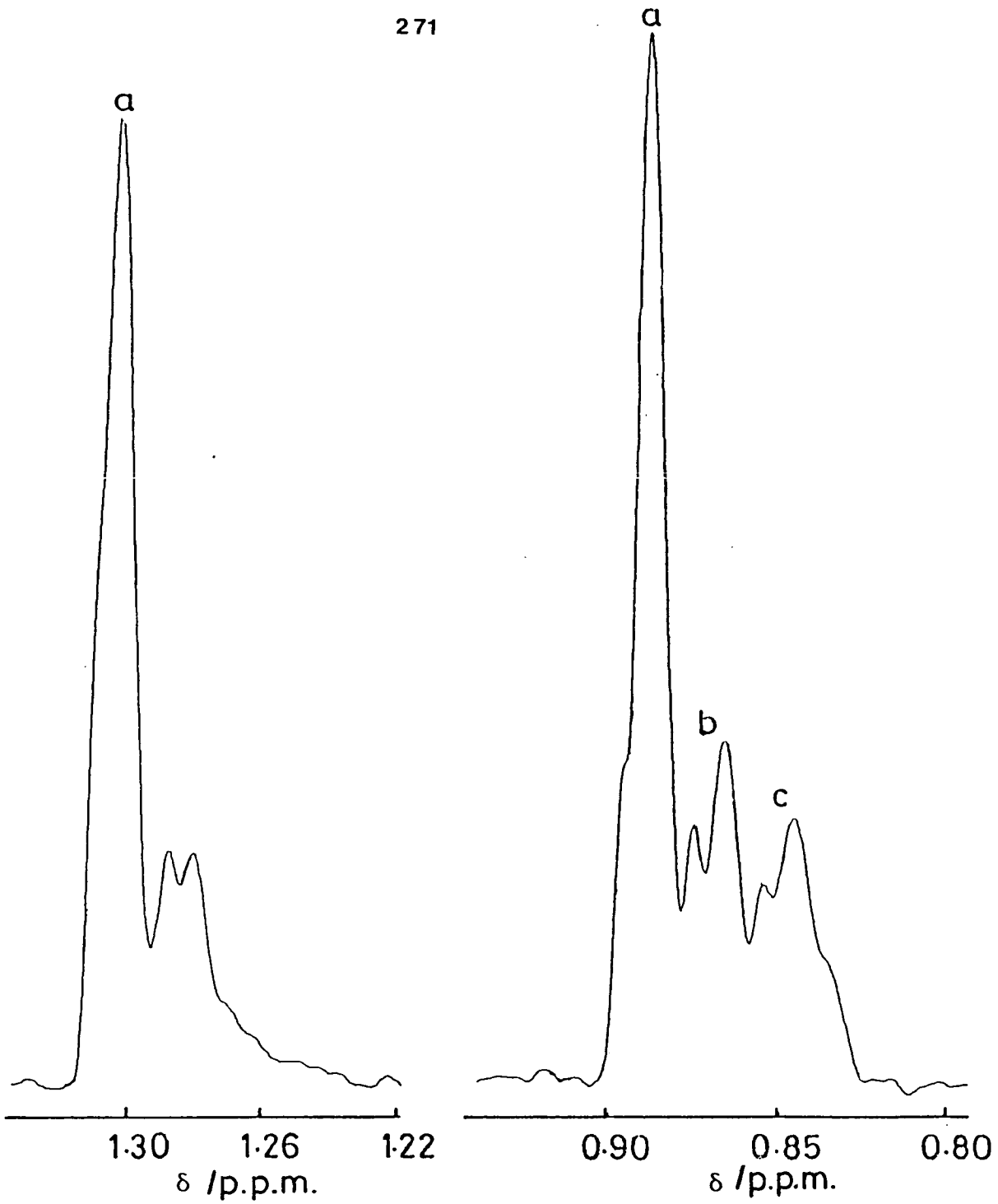


Figure 7.4 The nmr spectra for the secondary and primary D atoms in propane formed in the experiment Pt6. Peaks a correspond to the grouping $-CHDCH_2D$, b to the groupings $-CH_2CHD_2$ and $-CHDCHD_2$, c to $-CH_2CD_3$ and $-CHDCD_3$; the bulge to the right of this latter peak is due to $-CD_2CD_3$.

Table 7.2

Experimental Details and NMR Analyses of the Distribution of Deuterium in Propene and Propane over Platinum Catalysts

Experiment	Pt5(LTR)		Pt6[a]			
Catalyst mass/mg	54.7		9.1			
time/min	89		7			
T/K	233		236		198	293
alkane %	16.2		40		-	-
D in alkene						
CH_3-CD-CH_2	4.7	(30)[b]	1.1	(19)[b]	(28)[b,c]	(27)[b,d]
CH_3-CH=CHD(*cis*)	3.7	(23)	1.5	(25)	(27)	(13)
CH_3-CH=CHD(*trans*)	4.1	(26)	2.3	(37)	(42)	(39)
-CH_2D	3.3	(21)				
-CHD_2	-		1.2	(20)	(2)	(21)
-CD_3	-					
D in alkane						
2°D	36.9		38.8			
1°D						
-CH_2CH_2D			4.5			
-$CHDCH_2$D			23.8			
-CH_2CHD_2			3.9			
-$CHDCHD_2$	47.3		8.3			
-CH_2CD_3			3.1			
-$CHDCD_3$			7.5			
-CD_2CD_3			2.5			

a Pt/SiO_2.

b Figures in brackets are D in alkene expressed as percentage of total D in alkene.

c From ref. (17) at similar extent of propene exchange.

d From ref. (9) at similar extent of propene exchange.

having a deuterium neighbour so that d/h = 0.28 for the methylene positions. Comparison of the relative peak heights of $-CH_2D$ and $-CHD_2$ along the lines in table 6.3 gave d/h = 0.33 for the methyl positions, implying a similar extent of exchange had occurred in both groups.

7.3.2 Mass Spectrometric Analyses

Representative analyses of the final reaction products from the 2-methylpropene experiments for each of the four metals at 233 or 235K are shown in table 7.3. Reliable analyses were obtained for Pt1 and Ir1 because alkene exchange was not extensive and no alkenes were formed with less than two D atoms. The values for the alkenes in parentheses included for Ir1 and Rh2 are those obtained by using 9 eV electrons. With Rh2 the method of analysis was less satisfactory because some highly exchanged alkene was formed and the interpretation of the nmr data which will be presented later in section 7.4 indicated that some d_0- and d_1-alkane must have been present. These factors meant that the simple treatment to attribute the peaks at m/e = 58 and 59 to alkene and the peak at m/e = 60 to alkane was not correct. No problem was encountered with Rh3 because the conversion to alkane was complete. The results with Pd1 were the least accurate because of the very extensive exchange of the alkene. There was no simple method of deciding what fraction of the peaks in the range from m/e = 58 to m/e = 63 was attributable to alkanes. An

Table 7.3

Mass Spectrometric Analyses of the Isotopic 2-Methylpropenes and 2-Methylpropanes Corresponding to Samples Examined by NMR

	m/e	56	57	58	59	60	61	62	63	64	65	66	67	68
expt.	D_i (alkene)	D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8				
	D_i (alkane)			D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}
Pt1	alkene	83.4	2.2	0.6	-	-	-	-	-	-				
	alkane			-	-	11.4	1.3	0.5	0.7	-	-	-	-	-
Ir1	alkene	85.9	0.6	0.3	-	-	-	-	-	-				
	alkene (9eV)	86.5	0.3	0.1	-	-	-	-	-	-				
	alkane			-	-	20.1	1.7	0.8	0.5	-	-	-	-	-
Rh2	alkene	76.3	1.8	0.7	0.3	-	-	-	-	-				
	alkene (9eV)	77.1	1.3	0.4	0.2	0.2	-	-	-	-				
	alkane			-	-	9.1	5.1	2.0	1.1	1.5	0.2	0.2	1.0	0.7
Rh3	alkane			15.3	14.9	28.7	13.0	8.5	4.7	3.7	3.5	3.3	2.7	1.7
Pd1	alkene	22.8	27.5	18.1	8.2	2.7	1.0	0.3	0.2	-				
	alkane (approx. values)			-	-	(12)	(5)	(2)	(1)	(0.2)				

approximate analysis was made by calculating the fraction of the sum of these peaks attributable to alkane to give the total percentage of alkane equal to the value obtained by gas chromatography and arbitrarily assuming that the same fraction applied to each individual peak. The results for the alkenes which are more reliable than those for the alkanes did show that a range of isotopic alkenes were formed.

The deuterium distributions estimated for propene and propane using the calculations outlined in the experimental section 7.2, are given in table 7.4. The less reliable figures are given in parentheses but the amounts show that as well as a range of isotopic alkenes being formed there were reasonable amounts of d_0- and d_1-propane present.

7.3.3 Rates

Although the emphasis of this study was on the mechanistic aspects of the exchange and addition reactions of deuterium with the alkenes over the supported metal catalysts sufficient data from the analyses was accumulated so that some observations could be made on the course of reactions with time. Figure 7.5 shows results for Rh1 and Rh2, experiments in which the gases, by allowing the reactants to by-pass the catalyst, were exposed to the catalyst for a series of short periods with analysis by gas chromatography at the end of each period.

Table 7.4

Mass Spectrometric Analyses of the Isotopic Propenes and Propanes Subsequently Examined by NMR

	m/e	44	45	46	47	48	49	50	51	52	53	54
experiment	D_i(alkene)	D_0	D_1	D_2	D_3	D_4	D_5	D_6				
	D_i(alkane)			D_0	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8
Pt5(LTR)	alkene	78.5	4.1	(0.9)	(0.3)	-	-	-				
	alkane			(0.6)	(2.2)	8.9	2.8	1.1	0.6	-	-	-
Pt6	alkene	56.2	2.5	(0.9)	(0.4)	-	-	-				
	alkane			(1.8)	(5.5)	21.7	6.0	2.5	1.0	0.7	0.5	0.2

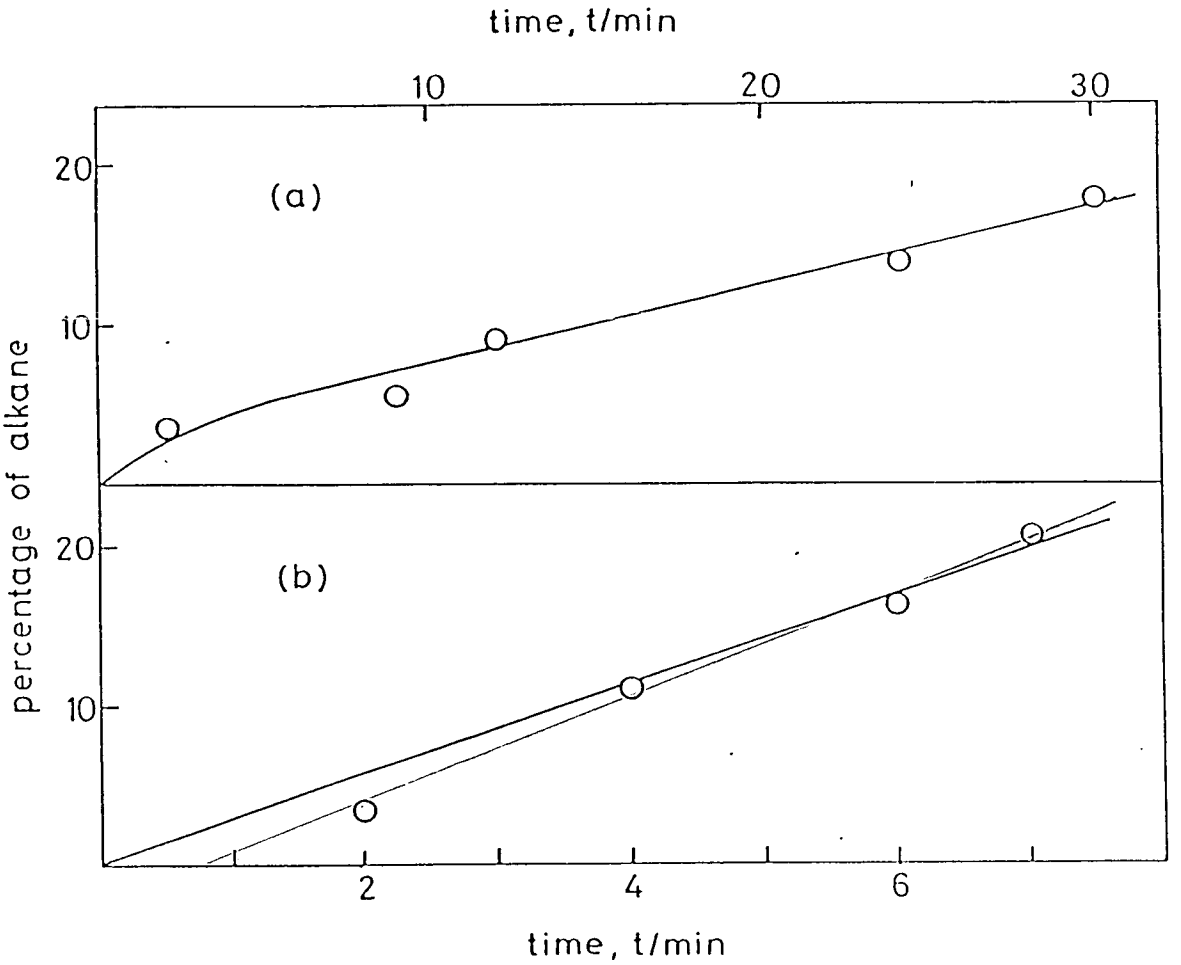


Figure 7.5 The course of the addition reaction with 2-methylpropeneand deuterium over Rh/SiO_2 by using exposure of the gases to the catalyst for short periods; (a) at 205K with 29 mg catalyst; (b) at 235K with 6 mg catalyst.

There was evidence for an initial rapid conversion at 205K followed by a steady rate of reaction. The results of 235K not surprisingly show more scatter for the periods of exposure to the catalyst were short. Most of the experiments showed some evidence of an initial burst of activity, but rates could be determined from the subsequent part of the reaction which produced alkane at a steady rate or at a rate which decreased slightly with time.

More detailed results could be obtained in experiments in which the mass spectrometric analyses of the alkenes by using 9 eV electrons were made through the course of the reaction. The course of experiment Pt3 is shown in figure 7.6 which includes the increase in the percentage of total alkene exchanged as well as the increase of D in the alkene. The latter was measured by $\phi = \Sigma i D_i$ where D_i is the percentage of the total alkene containing i deuterium atoms. The ratio of the gradients of these two curves associated with exchange gave a value of M, the mean number of deuterium atoms acquired by each molecule undergoing exchange . Where kinetic data were not available an approximate value of M was obtained from the average number of deuterium atoms in the exchanged alkene molecules, M_x, obtained from the mass spectrometric analyses such as those given in table 7.3. Rates of formation of the addition products, expressed in terms of the total amount of metal present and ignoring dispersion,

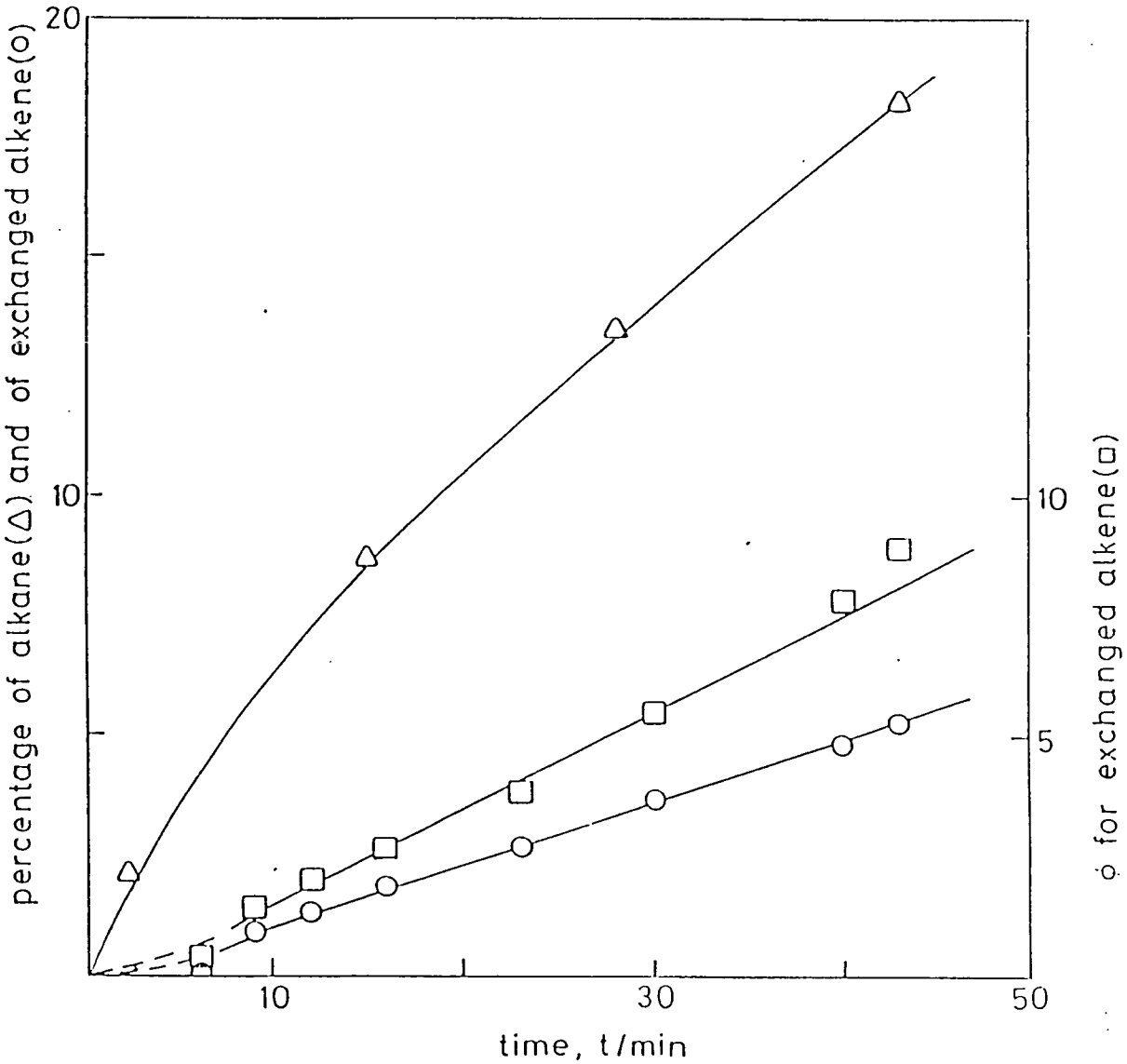


Figure 7.6 Course of the reaction of 2-methylpropene with deuterium in experiment Pt3(LTR)

Table 7.5

Rates of Formation of Alkane

Experiment	T/K	alkene[a]	D_2/alkene	Rate[b]
Pt1(LTR)	233	2MP	5	13
Pt2(LTR)	235	2MP	1	1.7
Pt3(LTR)	295	2MP	5	63
Pt4(HTR)	295	2MP	4	4.7
Pt5(LTR)	233	P	4	3.9
Pt6	236	P	5	409
Rh1	205	2MP	5	130
Rh2	235	2MP	5	300
Ir1	235	2MP	5	100
Pd1	233	2MP	5	53

[a] 2MP is 2-methylpropene and P, propene.

[b] units for this column are 10^3r per molecule per second per metal atom.

Table 7.6

Interpretation of the NMR and MS analyses, and the Distribution of Deuterium in the 2-Methylpropenes

expt.	Pt1(LTR)	Pt2(LTR)	Pt3(LTR)	Pt4(HTR)	Rh1	Rh2	Rh3	Ir1	Pd1
tertiary D/alkane	1.00	0.90	0.80	0.85	0.77	0.70	0.69	1.00	0.35
primary D/alkane	1.32	1.16	1.51	1.64	1.67	1.72	2.17	1.15	1.52
total D/alkane (NMR)	2.32	2.06	2.31	2.49	2.44	2.42	2.86	2.15	1.87
total D/alkane (MS)	2.32	(2.40)	(3.15)	(3.49)	(3.04)	(3.64)	2.83	2.20	(2.68)
DISTRIBUTION IN ALKENES									
preferential exchange CX_2/CX_3	4.2	2.2	1.8	1.7	3.8	3.0	-	-	1.0
D/CX_2 group	1.00	1.09	1.15	1.08	1.15	1.25	-	-	1.11
D/CX_3 group	1.00	1.08	1.17	1.09	(1.0)	1.25	-	-	1.26
M or M_X	1.2	1.3	1.8	1.5	1.4	1.6	-	(1.2)	-
Groups exchanged per molecule	1.2	1.2	1.5	1.4	(1.3)	1.3	-	-	-

are given in table 7.5. Values of M or M_x are included in table 7.6.

7.4 INTERPRETATION OF RESULTS

The nmr results in table 7.1 provide information on the relative amounts of deuterium present in the various groupings in the 2-methylpropenes and in the tertiary and primary positions of the 2-methylpropanes in the samples analysed at the end of each experiment. These numbers were converted to absolute values by examining the detailed nmr spectra for the primary deuterium atoms in the alkane. In each experiment it was possible to estimate the average fraction of tertiary D per alkane molecule by estimating the relative amounts of the groupings CH_2DCD and CH_2DCH, CHD_2CD and CHD_2CH, and CD_3CD and CD_3CH. Results derived in this way are shown in table 7.6. A different procedure was necessary for the results over palladium because of the overlap between the nmr resonances for $-CD_3$ in the 2-methylpropene and for the tertiary D in the 2-methylpropane. It was found that the distribution of deuterium in the various groupings in the alkene was close to a random distribution as shown in table 7.7, with a chance of d = 0.20 of a D atom in each position, i.e. 1.60 D atom/alkene in total. A simple calculation based on this value indicated that the 9.0% of deuterium in the combined peak had to be divided into 4.9% for $-CD_3$ in the alkene and 4.1% for tertiary D in the

alkane in order to obtain tertiary D/alkane = 0.35 in agreement with the value estimated from the nmr peaks for the primary deuterium in the alkane.

Table 7.7
Distribution of Deuterium in the Alkene After Reaction in Experiment Pd1

Grouping	=CD	$=CD_2$	$-CH_2D$	$-CHD_2$	$-CD_3$
experimental	19.3	4.9	46.6	22.9	6.3[a]
calc. (d=0.20)	20.0	5.0	48.1	23.8	3.1

(a) Assuming that the 9.0% in table 1 consisted of 4.9% $-CD_3$ in the alkene and 4.1% tertiary D in the alkane, see text.

The values of total D/alkane based on the nmr analysis were in good agreement with the mass spectrometric (MS) results in all cases except for Ir1 where the signals for deuterium in the 2-methylpropene were too weak to be estimated and for Pd1 where the MS analyses were obviously unreliable because of the overlap between the alkene and alkane spectra. On the other hand, the results for total D/2-methylpropane from the nmr analyses only agreed with the MS values for Pt1, Rh3 and Ir2. For all the other experiments, the MS results gave too high a value which indicated that the neglect of d_0- and d_1-alkane in the interpretation of the mass spectrometric results was not justified.

Further information about the exchanged 2-methylpropenes is collected in the lower part of table 7.6. In all experiments there was preferential exchange of the methylene of the alkene, except over Pd which gave random exchange of all positions as already mentioned. Again, apart from Pd, the average deuterium content of the exchanged methylene and methyl groups of the alkenes were almost the same in each experiment. The number of groups, methylene or methyls, exchanged in each reacted alkene ranged between 1.2 and 1.5 with the higher values observed in the platinum runs at 295K.

Further details about the distributions of deuterium in the 2-methylpropenes derived from the analyses are brought together in table 7.8. The average deuterium content of the exchanged methyl groups, D/CX_3, was calculated from the nmr spectra and when combined with the average primary deuterium content of the alkane gave the numbers of the different types of methyl groups shown in table 7.8. The results for Rh2 can be used to illustrate these calculations. Values in table 7.1 show the relative amounts of primary D in the methyl groups CH_2D, CHD_2 and CD_3 were 26.3:21.7:18.8. It follows that the relative proportions of these groups were 26.3/1:21.7/2:18.8/3 and the average D content of the exchanged groups was 1.54. To account for the 1.72 primary D/alkane, the average number of exchanged groups per molecule was 1.72/1.54 = 1.12 and thus the number of CH_3 groups was 3-1.12 = 1.88.

Table 7.8

Distribution of Deuterium in the 2-Methylpropanes and Other Results from the Analyses

expt.	Pt1(LTR)	Pt2(LTR)	Pt3(LTR)	Pt4(HTR)	Rh1	Rh2	Rh3	Ir1	Pd1
D/CX_3 in alkane	1.20	1.18	1.35	1.37	1.50	1.54	1.67	1.10	1.33
No. of groups									
$-CH_3$	1.90	2.02	1.88	1.80	1.89	1.88	1.70	1.97	1.88
$-CH_2D$	0.94	0.85	0.83	0.88	0.72	0.68	0.68	0.92	0.85
$-CHD_2$	0.10	0.08	0.18	0.20	0.23	0.28	0.37	0.11	0.21
$-CD_3$	0.06	0.05	0.10	0.12	0.16	0.16	0.25	-	0.08
exchanged D/alkane (g)	0.32	0.26	0.71	0.79	0.90	1.02	1.48	0.15	1.17
2g/f	17	7.2	16	7.2	35	50	-	(50)	1.5
addition (g) / exchange	3.8	2.4	2.0	0.9	3.6	5.1	-	(46)	0.1
% in D_2	0.8	4.1	1.4	3.8	1.2	1.3	12.0	1.3	13.2

The exchanged D/alkane, g, was the extra deuterium present over and above the amount added in conversion of alkene to alkane, assuming that the chance of acquiring primary D was identical with the tertiary D found. For example in experiment Rh1 with primary and tertiary D/alkane of 1.67 and 0.77 atom/molecule respectively, the exchanged D/alkane was 0.90 = 1.67-0.77. The next row in the table gives the ratio of exchanged D/alkane to the mean deuterium content of the alkene throughout the experiment, 2g/f. This value provided a measure of the extent to which the deuterium content of the alkane was greater than that expected simply from the addition of two atoms to the alkenes. The fact that most values were significantly greater than 1.0 showed that either further exchange was occurring in the addition reaction or that the composition of the alkene that underwent conversion to alkane was richer in deuterium than the average for the total alkene, i.e. adsorbed and gas phase. The ratio q, which was obtained by dividing the percentage conversion to alkane by ϕ, the mean number of deuterium atoms per 100 molecules of alkene, provided an approximate estimate of the relative ratio of addition to exchange. Finally, the %H in the deuterium at the end of each experiment was obtained by mass balance calculation.

By using a combination of the mass spectral and nmr data similar estimates could be made for the propane produced from propene addition over the Pt/SiO_2 catalyst,

experiment Pt6. From the mass spectral data the average deuterium content of the alkane was 2.28 which could be further divided into 0.98 secondary D and 1.30 primary D from the information given in table 7.2. This implies an excess of 0.30D per alkane molecule over and above that expected from straightforward addition. Addition was 4.7 times faster than alkene exchange.

7.5 DISCUSSION

The results in table 7.5 show that for the conversion of 2-methylpropene to alkane at 235K the relative activities of the metals were Rh>Ir>Pd>Pt, but the spread of activity was only a factor of about 20. The lower rate for Pt2 in comparison with Pt1 was consistent with an approximate first-order dependence of rate on the pressure of deuterium. The reduction of rate by a factor of only 13 at 295K from Pt3(LTR) to Pt4(HTR) showed that strong metal-support interactions were not causing a very marked change in the catalytic properties of the platinum and the differences in the character of the reactions as shown by the various results in tables 7.1, 7.6, and 7.8. This is not surprising due to the reported structure-insensitivity of alkene addition reactions. The change in support, however, shown by the difference in rates of the two propene reactions, did have a significant effect. If allowance is made for the different dispersions of the two platinum catalysts, the silica supported sample proved to

be 35 times more active than the niobia supported catalyst. This in part may have been caused by self-poisoning of the Pt/Nb_2O_5 catalyst where the experiment was originally commenced at 205K before increasing the temperature to 233K in order that the desired amount of addition was obtained. After allowing for a first order dependence in hydrogen, the rate obtained for the Pt/SiO_2 catalyst, experiment Pt6, was of a similar magnitude to that reported by Naito and Tanimoto[17].

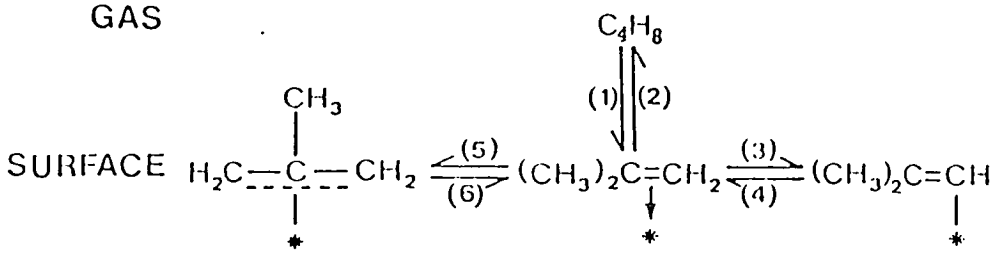
Comparisons can be made between the present results for the reactions of 2-methylpropene with information in the literature for the reactions of other alkenes, such as ethene and propene, on the same four metals. Bond and Wells[1] gave details for the reactions of both ethene and propene with deuterium over a number of supported metals, including those used in this work. Exchange was found to be faster than addition with palladium and considerable dilution of the surface deuterium with hydrogen occurred so that appreciable amounts of alkanes containing less than two deuterium atoms were formed. The results with palladium conform to this behaviour. Likewise, there is agreement that iridium gives the smallest rates of exchange to addition with all three alkenes and that rhodium shows rather more exchange than platinum.

The earlier work reviewed by Bond and Wells[1] interpreted the results with ethene and propene solely in

terms of associative mechanisms, but considerable evidence published since then has indicated the importance of dissociative mechanisms for the exchange and isomerisation of propene and larger alkenes[6,9,11,12,13]. Before continuing discussing the results, it would be helpful to consider the various types of reaction which might operate with the 2-methylpropene/2-methylpropane systems and the consequences of each of them for alkene exchange or addition.

7.5.1 Possible Mechanisms

Either of the dissociative reactions shown in scheme 7.1 might contribute to alkene exchange. Steps (1) and (2) combined with (3) and (4) would give replacement of one or both of the hydrogen atoms in the methylene group of the alkene, but no exchange in the methyl groups. Complications from isotope effects have to be considered at the temperatures used for the experiments. Results previously published[25,26] show that the rate of dissociation of C-H bonds occurs at least a factor of 10 more rapidly than the corresponding reaction for C-D bonds at temperatures such as 235K. Thus repetition of steps (3) and (4) will lead to a greater proportion of $(CH_3)_2C{=}CD_2$ than would be expected if random replacement occurred without any kinetic isotope effect.

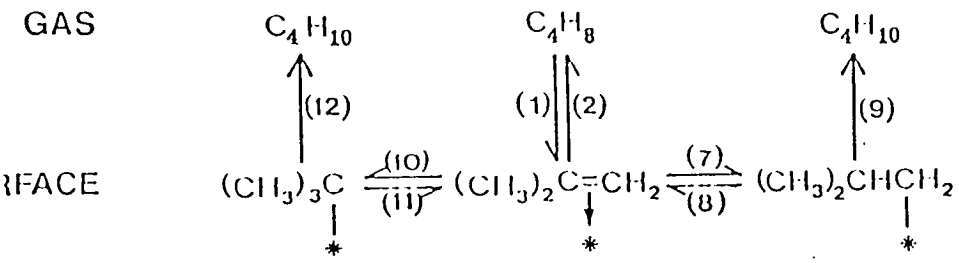


Scheme 7.1 Possible dissociation reactions that may contribute to the exchange of 2-methylpropane.

Steps (1) and (2) combined with (5) and (6) would lead initially to exchange in a methyl group, but subsequently to the replacement of any of the eight hydrogen atoms in the alkene. Steps (5) and (6) can also provide a means of double-bond movement without further exchange by loss and gain of an H atom; this type of reaction will be relatively rapid because of the isotope effect.

In the associative reactions, shown in scheme 7.2, steps (7) and (8) lead neither to exchange of the alkane nor do they provide a means of obtaining enhanced exchange of the alkane over and above the simple addition corresponding to steps (7) and (9). The combination of steps (1) and (2) with (10) and (11) can give alkene exchange, initially in either the methylene group or the methyl group, but subsequently in all positions, so that the overall results should be similar to those described for the dissociative mechanism involving steps (5) and (6) in scheme 7.1. Steps (10) and (11) can also contribute to further exchange of the alkane to give products containing more deuterium than expected just from the addition steps (10) and (12). However, unless there is some degree of

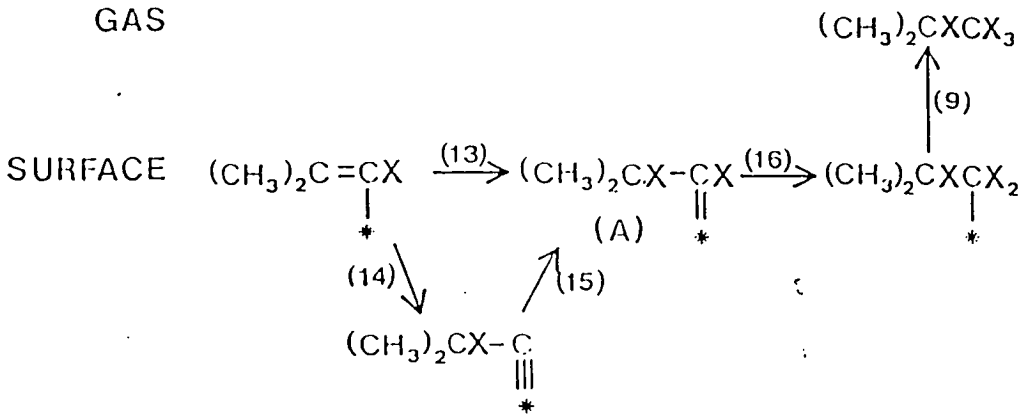
restricted rotation of the 2-alkyl species formed by step (10) further exchange associated with the repetition of steps (10) and (11) would be spread over the three methyl groups of the alkane and not concentrated in one such group. Other mechanisms have to be considered to account for the experimental results that, as will be shown later, indicate that the additional exchange of the alkane tends to be concentrated in a single methyl group.



Scheme 7.2 Associative reactions of 2-methylpropene that provide routes to alkane and might contribute to exchange of alkene by steps (10) and (11).

It is probable that the most highly exchanged methyl group in the alkane derives from the methylene group of the alkene and two possible ways for this to happen are shown in scheme 7.3. Step (13) involves an acquisition of an atom (H or D) at the central carbon atom of the adsorbed vinyl species to form intermediate A. The alternative route gives an alkylidyne species by isomerisation of the vinyl in step (14) and then conversion to A through step (15). Further reaction of A by step (16) leads to the 1-alkyl adsorbed intermediate which will then form an alkane with enhanced exchange in

one methyl group.



Scheme 7.3 Possible routes from vinyl to alkyl intermediates leading to enhanced exchange of one methyl group of the alkane. X represents H or D.

7.5.2 Deuterium Distributions and Choice of Mechanisms

7.5.2.1 Platinum and rhodium

Both of these metals showed preferential exchange, more marked at lower temperatures, in the methylene group of the alkene. Another important feature of the results in table 7.8 is that the extent of the exchange in the methyl groups which had acquired deuterium was identical with the extent of the exchange in the methylene group. This was also the case for exchanged propene from experiment Pt6 as indicated earlier. Thus these results give a strong indication that the principal mechanisms are exchange through the vinyl dissociative route, steps (3) and (4), combined with an isomerisation that converts the methylene group into a methyl group through H atom transfer via the π-allyl intermediate. This isomerisation must be mainly intramolecular in that the H atom

dissociated is the H atom acquired and further exchange does not occur to an appreciable extent.

The values of M, which ranged from 1.2 to 1.6, were higher for rhodium than platinum and tended to be larger with increase of temperature. It follows that step (3) cannot be much faster than step (2) because of the limited extent of multiple exchange. The results in table 7.6 also demonstrate that the majority of the exchanged alkene molecules possessed either an exchanged methylene group or an exchanged methyl group, except for the higher-temperature results with platinum where the number of exchanged groups per molecule increased to 1.4 or 1.5. These facts are in accord with the mechanisms suggested.

Addition to form alkane, see table 7.8, was noticably faster than exchange on rhodium and on platinum, except for the special case of platinum at 295K subjected to HTR. But the most striking feature of the results was the evidence that alkane formation was accompanied by further exchange which was mainly concentrated in one methyl group as shown by the results in table 7.8. Significant amounts of $-CD_3$ groups were detected in the alkanes formed over rhodium and to a lesser extent with platinum and the average number of exchanged methyl groups per alkane was usually in the range from 1.0 to 1.2, rising only to 1.3 in the special case (Rh3) where all the alkene had been converted to alkane. These results are not consistent with alkyl reversal, steps (10) and (11), as the mechanism

for the exchange accompanying addition. Such a mechanism would tend to exchange more of the methyl groups to a limited extent rather than one methyl group to a marked degree unless there was some measure of restricted rotation of the adsorbed 2-alkyl species such that repeated exchange of a single methyl group was favoured. However the mechanisms outlined in scheme 7.3 are the preferred means by which further exchange associated with one methyl group of the alkane is achieved. As has been shown in the previous two chapters of this work, rhodium is somewhat better than platinum at forming $\alpha\alpha$-diadsorbed species from hydrocarbons and so it is not surprising that it shows the greater amount of further exchange associated with alkane formation even at comparatively low temperatures.

These calculations about the mechanisms for the reactions of 2-methylpropene and propene differ from those given by Naito and Tanimoto[17] for the reactions of propene over Pt/SiO_2. They suggested that dissociative mechanisms operated only in the absence of added hydrogen or deuterium, i.e. for reactions such as the exchange between C_3H_6 and C_3D_6. Although the conclusions from the propene results are less clear it is believed that dissociative mechanisms are essential to account for the results with 2-methylpropene. They argued for exchange by an associative mechanism in the reaction of C_3H_6 with D_2 on the grounds that both exchange and addition had the same

activation energy and the same kinetics. But to explain the selective nature of the exchange they were forced to assume that the two methyl groups in the 2-alkyl intermediate were not identical. It is possible that the identity of activation energies and kinetics for exchange and addition may be a coincidence and that the preferential exchange of various vinyl hydrogens in propene arises through dissociative mechanisms and not from some restricted rotation of the 2-alkyl intermediate in an associative mechanism. The small extent of exchange in the methyl group of the propene observed by Naito and Tanimoto, and also in this work, is difficult to explain if an associative mechanism operates. On the other hand, there is agreement with them on the need to have an intramolecular mechanism for isomerisation to account for the changes in the distribution of deuterium atoms in the propene molecules as reaction proceeds.

7.5.2.2 Iridium

The rate of exchange was small and exchanged alkene was not formed in sufficient quantity for nmr analysis. The results in tables 7.3 and 7.8 show that the major product of the addition reaction was d_2-alkane but a small amount of further exchange also occurred and, as with rhodium and platinum, this was confined to one methyl group of the alkane.

7.5.2.3 Palladium

The results with palladium differed substantially from those with the other metals. The exchange reaction was 10 times faster than the addition process. The distribution of deuterium in the alkene was random apart from a slight excess of $-CD_3$ presumably as a consequence of the kinetic isotope effect. Either of the mechanisms leading to random distributions, i.e. π-allyl through steps (5) and (6) or alkyl reversal through steps (10) and (11), might be operating and a choice has to be made on other grounds. An important point is that, with palladium, the amount of deuterium in the alkane was close to the value expected for addition of two atoms to the alkene without further exchange, as shown by the value of 2g/f in table 7.8. This suggests that alkyl reversal may be less important than the π-allyl mechanism for the exchange of the alkene. The efficient exchange of the alkene implies that step (2), alkene desorption, is a relatively fast reaction over palladium. The ease of alkene desorption is, of course, one of the factors which makes palladium a good catalyst for the selective hydrogenation of alkynes. The rapid exchange that occurred with palladium led to the most substantial dilution of the deuterium surface pool with hydrogen so that the chance of acquiring a D atom was only 0.35. Desorption of H_2 and HD must be relatively slow reactions because a comparison of the results in table 7.6 and 7.8 show that the chance of acquiring a D atom,

measured by the amount of tertiary D in the alkane, was less than expected from the composition of the hydrogen/deuterium gas. This observation applied to most of the results with rhodium and platinum as well as for palladium. Naito and Tanimoto[16] showed that exchange was faster than addition for the reaction of propene and deuterium over Pd/SiO_2 and they found that selective exchange was followed by an intramolecular double-bond migration leading to a more random distribution in the alkene. These results with 2-methylpropene are broadly similar to their findings with propene but, as indicated above, the emphasis that they place on associative mechanisms for the exchange of the alkene is doubtful.

7.6 CONCLUSIONS

1. Deuterium nmr spectroscopy proved to be a good technique for use with the 2-methylpropene/deuterium system. The detailed information, so obtained, on the distribution and grouping of deuterium atoms in the products is helpful in identifying intermediates and mechanisms for the reactions on metal catalysts.
2. Palladium shows a preference for exchange of alkene rather than addition and leads to a random distribution of the deuterium in the alkenes.
3. Addition is much faster than exchange with iridium and somewhat faster with rhodium and platinum.
4. Clear indications of a role for exchange through a

dissociative mechanism involving adsorbed vinyl intermediates are found from the distribution of products from the 2-methylpropene reactions over rhodium and platinum.

5. Double-bond migration through an intramolecular π-allyl intermediate is indicated for palladium.
6. Further deuterium is introduced, largely into one methyl group when alkene is converted to alkane over iridium, platinum and particularly rhodium. Mechanisms other than the usual alkyl reversal processes are required to account for these results.

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